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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				
INTERNATIONAL APPLICATION NO. PCT/JP00/03048		INTERNATIONAL FILING DATE 12 May 2000		PRIORITY DATE CLAIMED 26 May 1999
TITLE OF INVENTION METHOD OF PRODUCING TOWN GAS				
APPLICANT(S) FOR DO/EO/US Ishigaki, Shinya et al.				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 				
Items 11 to 20 below concern document(s) or information included:				
<ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Other items or information: 				
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Nov. 15, 2001				

Patent
Attorney Docket 4353

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Application No.: PCT/JP00/03048)
)
Filed: May 26, 1999)
)
For: METHOD OF PRODUCING)
TOWN GAS)

Pittsburgh, Pennsylvania

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly amend the specification and claims as indicated hereinafter.

In the specification:

Delete the paragraphs beginning at line 7 on page 1 and ending on line 29 of page 5 and substitute therefore the following amended paragraphs:

-- Background Art

Recently, in the major cities, town gas is obtained by evaporating liquefied natural gas (LNG). However, to produce town gas from LNG requires the facilities for maintaining the received LNG at an extremely low temperature under -162°C and for evaporating the LNG to

produce town gas. Accordingly, it is not suitable for small or medium-sized businesses to produce town gas from LNG. Further, it is forecast that LNG will become scarce as a resource in the near future. Accordingly, it is desired that town gas be made from feed stock other than LNG or, from substitute natural gas (SNG). Accordingly various methods for producing town gas have been proposed.

① Methods using hydrocarbons as feed stock;

There are methods for producing town gas from hydrocarbons, such as liquefied petroleum gas (LPG) and naphtha. Japanese Patent Publication No. 51134/1987 discloses a method for producing gas containing methane (CH_4) as a main component, hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO), by means of steam reforming of hydrocarbons of carbon number 2 to 14 with the catalyst containing nickel, cerium and alumina. And Japanese Patent Opening Gazette No. 144089/1980 discloses a method for producing gas containing methane as a main component, by means of steam reforming of heavier hydrocarbons with the catalyst containing ruthenium. Further, Japanese Patent Opening Gazette No. 17003/1987 discloses a method for producing gas containing methane as a main component, by means of steam reforming of desulfurized hydrocarbons with the catalyst containing ruthenium.

② Methods using alcohols as feed stock;

There are methods for producing town gas from alcohols, such as methanol (CH_3OH) or a mixture of methanol and water (H_2O). Japanese Patent Publication No. 24835/1982 discloses a method for producing fuel gas of higher heating value where a gas containing methane, hydrogen, carbon dioxide and carbon monoxide, is produced by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium, followed by methanation of the produced hydrogen and carbon monoxide. And Japanese Patent Opening Gazette No. 156196/1987 discloses a method for producing methane by a single step by

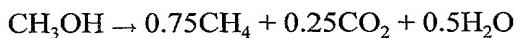
contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium and lanthanum as essential components.

Further, Japanese Patent Opening Gazette No. 234499/1989 discloses a method for efficient evaporation of liquid phase methanol and water, which are heated by the heat of outlet gas of a reactor and are contacted directly with recycled gas. Japanese Patent Opening Gazette No. 304184/1989 discloses a method for separating carbon dioxide from gas produced by the reaction between alcohol and steam, using liquid phase alcohol. Japanese Patent Opening Gazette No. 123737/1991 discloses a reactor of the type which recovers reaction heat to utilize this evaporation and preheat of feed stock.

And, we have not been able to find out the Prior Art regarding a method for producing town gas from dimethyl ether as feed stock.

The above methods ① using hydrocarbons as feed stock require the facilities for desulfurization, supply of hydrogen used for the desulfurization, and hydrogen recycle, since such hydrocarbons as naphtha contain sulfur compounds. Further, sulfur in hydrogen sulfide produced on desulfurization process, is generally fixed as zinc sulfide. It cannot help in treating the zinc sulfide as industrial wastes since zinc sulfide is difficult to decompose and reuse, which causes environmental problems in the future.

The above methods ② use methanol as feed stock in many cases. Since methanol has been desulfurized in the course of production, desulfurization facilities are not newly required in these methods. In this respect, these methods are superior to the above methods using hydrocarbons as feed stock. However, producing town gas from methanol is carried out according to the following reaction equation, theoretically;



That is, 0.75 mol carbon element in CH₃OH is converted into CH₄, and 0.25 mol of that are converted into CO₂. At this time, 0.5 mol of H₂O (water corresponding to 28% of the weight of methanol) is also produced. In point of transportation of feed stock, it is not economical since potentially reproduced water, not being fuel, is transported. Further, on the production of town gas, it is needed to evaporate the water when evaporating methanol. Accordingly, energy is unnecessarily consumed. Furthermore, it requires liquefied petroleum gas as carburant to make the town gas.

Accordingly, it is an object of this invention to provide a method for producing town gas, in which a sulfur component is not contained in the feed stock, so desulfurization facilities are unnecessary, and cryogenic storage facilities are also unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and liquefied petroleum gas is unnecessary as carburant, and which is suitable for small or medium-sized businesses to carry out.

Disclosure of Invention

The above object can be solved by the method for producing town gas, as a first claim of the present invention; using dimethyl ether (CH₃OCH₃ or C₂H₆O) as feed stock, and evaporating the dimethyl ether, and reforming the dimethyl ether catalytically under the existence of steam, and producing gas mainly containing methane.

The dimethyl ether used for feed stock can be crude dimethyl ether containing, alcohols which contain methanol as a main component, and/or water. Such a method for producing town gas is carried out according to the following reaction equation, theoretically:



Coexistent steam functions to suppress temperature rise of the reaction system.

It is evident from the above reaction equation that 0.75 mol of carbon element in 1 mol C_2H_6O is converted into CH_4 , and 0.25 mol of that are converted into CO_2 , which is similar to the case using methanol as feed stock. However, this method using dimethyl ether is efficient and advantageous from the view of transportation, since H_2O is not reproduced. Further, heat energy is not unnecessarily consumed on the evaporation process of the feed stock.

In a method for producing town gas, as a second claim of invention, the quantity of the steam for catalytic reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether. Necessary quantities of the steam is ordinarily obtained by means of introduction into the reaction system from outside. However, in the case wherein the dimethyl ether contains water beyond some quantity, the steam to be introduced from the outside may be unnecessary. The quantity of the coexistent steam to suppress the temperature rise of the reaction system is reduced and the consumption of heat energy is reduced in the method for producing town gas according to the present invention.

In a method for producing town gas, as a third claim of invention, the temperature for the catalytic reforming of the dimethyl ether is within 200 °C to 600 °C, and preferably within 250 °C to 550 °C. Such a method prevents deactivation of the catalyst caused by excess temperature rise of the reaction system.

In a method for producing town gas, as a fourth claim of invention, dimethyl ether is supplied to serially installed adiabatic fixed bed reactors, under the existence of steam, by one of the following manners;

- ① Passing cooling means installed between the reactors, dimethyl ether is supplied serially to the reactors;
- ② A part of divided dimethyl ether is supplied to the reactors serially, and at the same time, the remaining part of the divided dimethyl ether is supplied to the subsequent reactors.

Such a method suppresses excess temperature rise of the reaction system caused by heat of the reforming reaction in the case of using an adiabatic fixed bed reactor.

In a method for producing town gas, as a fifth claim of invention, dimethyl ether is reformed with a fluidized bed reactor or a multi-tubular reactor which is in the form of a single stage or plural stages. Such a method for producing town gas prevents excess temperature rise of the reaction system by simplified equipment.

In a method for producing town gas, as a sixth claim of invention, by-produced carbon dioxide is removed from the reformed gas of dimethyl ether. Such a method produces gas of higher heating value not containing incombustible gas.

In a method for producing town gas, as a seventh claim of invention, carbon dioxide is removed using any of the following manners;

- ① Absorption by aqueous alkanolamine solution or heated aqueous potassium carbonate solution;
- ② Adsorption by pressure swinging;
- ③ Selective separation by membrane.

Such a method positively removes carbon dioxide from the reformed gas.

In a method for producing town gas, as an eighth claim of invention, hydrogen, carbon monoxide and carbon dioxide, which are by-produced on the reforming process of dimethyl ether, are methanized either before or after removing carbon dioxide from the reformed gas. Such a method furthermore increases the heating value of the produced reformed gas.

In a method for producing town gas, as a ninth claim of invention, dimethyl ether used for feed stock is added to the produced reformed gas as carburant. Special facilities for storage or supply of carburant is unnecessary in contrast to such other carburants as liquefied

petroleum gas, and the heating value of product gas can be controlled so as to adjust to the standardization. - -

Delete the paragraphs on page 6 beginning at line 13 and ending in line 25 and substitute the following amended paragraph:

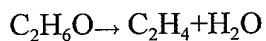
- - Conventionally, dimethyl ether is produced by dehydration of methanol which is produced in advance. However, in recent years, the dimethyl ether tends to be directly produced by the reaction between hydrogen and carbon monoxide as in the following equation;



In this reaction, CH_3OH is sometimes by-produced besides H_2O . In this invention, not only pure dimethyl ether but also crude dimethyl ether containing alcohols of which the main component is methanol, and/or water, can be used for feed stock. Since dimethyl ether does not contain sulfur components, similar to methanol, desulfurization facilities are unnecessary for the production of the town gas. Further, since the boiling point of dimethyl ether is -25.1°C , which is close to that of methanol, cryogenic storage facilities as needed for LNG, are unnecessary. - -

Delete the paragraphs beginning at line 26 on page 7 and ending at line 8 on page 9 and substitute therefore the following amended paragraphs:

- - The reforming reaction of the equation (1) is highly exothermic. Hence, when the temperature of the reaction system rises excessively, the reforming reaction of the equation (1) will not proceed toward the right side due to chemical equilibrium. Besides, there is a possibility of the side reaction which produces ethylene (C_2H_4) as in the following equation;



Ethylene deposits resinous material on the surface of the catalyst and prevents the reforming reaction. Accordingly, it is desirable to control the reaction temperature within the above temperature range by cooling the reaction system adequately. In this invention, steam coexists for reforming reaction of dimethyl ether. The principal purpose of coexistence of steam is to suppress the temperature rise of the reaction system.

However, the coexistence of the steam requires extra thermal energy for heating or cooling the steam, in the whole of the production process of the town gas. Accordingly, it is not economical that the quantity of the steam is beyond 10/1 mole ratio (steam/dimethyl ether), and the preferable quantity of the steam is under 10/1, and more preferably under a ratio of 5/1. However, it becomes difficult to suppress the temperature rise of the reaction system when the quantity of the steam is under a ratio of 0.5/1. Accordingly, a most preferable quantity of the steam is within a ratio of 1/1-2/1 in consideration of the steam quantity to be used and the ease of temperature control of the reaction system.

As a reactor used for the reaction process of reforming dimethyl ether catalytically, there can be used an adiabatic fixed bed reactor which has no internal cooling means. In this case, special considerations are required for keeping the reaction temperature within the preferable range.

For example, dimethyl ether is supplied to a plurally and serially installed adiabatic fixed bed reactor filled with catalyst, under the existence of steam, according to the following procedures; ① passing cooling means installed between the reactors, dimethyl ether is serially supplied to the reactors, or ② dimethyl ether is divided into two or more parts, and a part of the dimethyl ether is serially supplied to the reactors, and at the same time, the remainder of the dimethyl ether is supplied to the subsequent reactors.

Besides, when a fluidized bed reactor or a multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system is sufficiently cooled down. It may be used in a single stage. The fluidized bed reactor has a perforated plate under a fluidized layer of powdery catalyst. The powdery catalyst is fluidized by introduction of feed gas through the perforated plate and is cooled down by internal cooling means. The multi-tubular reactor has many reaction tubes filled with catalyst. The outside of the reaction tubes is formed as a jacket and is flowed with a medium for cooling the catalyst. In the case that the fluidized bed reactor or the multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system can be easily controlled with the coexistence of steam. - -

Delete the paragraph beginning at line 17 on page 9 and ending at line 24 of page 9 and substitute therefore the following amended paragraph:

- - Both reactions are reversible and absorbent can be regenerated.

② Adsorption by pressure swinging;

CO₂ is adsorbed on silica gel, molecular sieve or active carbon under higher pressure and desorbed under atmospheric or lower pressure.

③ Selective separation by membrane;

Only CO₂ can be separated selectively from the mixture of CH₄ and CO₂ by a membrane having a large permeability of CO₂, such as polyimide, cellulose ester, or polysulfon membranes. - -

Delete the first paragraph on page 12 beginning at line 1 and ending at line 10 and substitute therefore the following amended paragraph:

- - It is apparent from Table 1 that the latent heat of vaporization of dimethyl ether is smaller than that of methanol, and so the heat energy for vaporization of dimethyl ether is

smaller than that of methanol. Further, in the theoretical value of the product of methane per unit volume of transported liquid, dimethyl ether is larger than methanol. In this respect, dimethyl ether is superior to methanol as feed stock to be transported. Furthermore, the heat of dimethyl ether on reforming is greater. Accordingly, the heat of the reforming reaction can be used more efficiently for vaporization and heating of dimethyl ether as feed stock. As above described, it is more beneficial to use dimethyl ether as feed stock of town gas. --

Delete the paragraphs beginning at line 9 on page 13 and ending at line 13 on page 14 and substitute the following amended paragraphs:

- -The reason that the reforming reaction of DME is divided into two, by supplying DME into the first and second reforming reactor 15A, 15B together with the steam, is to prevent depositing resinous materials on the surface of the catalyst in the reactors and deactivation of the catalyst due to sintering, besides the fact that the reforming reaction of DME shown by the above equation (1) will not proceed toward the right side in chemical equilibrium when the temperature of the reaction system rises excessively with heat of the reforming reaction, which is an exothermic reaction. In this respect, reforming reactors may be installed serially as three or more. Further, in the case that DME contains enough water, a process flow which does not introduce the steam from outside, is applicable, omitting the water storage 14, the pump 14P and the conduits 1c, 1d from Fig. 1.

DME is supplied serially into the first and second reforming reactors 15A, 15B in the above. However, a part of the DME may be supplied serially into the first and second reforming reactors 15A, 15B, and at the same time, another part of the DME may be directly supplied into the second reforming reactor 15B.

Referring to Fig. 1, DME from the DME storage 11 is divided in two at a downstream point of the heat exchanger 12a. A part of the divided DME is heated at a top portion of the heating furnace 13 through a conduit 1h and then is supplied into the second reforming reactor 15B through the conduit 1g together with the outlet gas of the first reforming reactor 15A.

According to such a procedure, it is possible to better equalize the load distribution between the first and second reforming reactors 15A, 15B. Equalization of reaction temperature can be facilitated. Further, there can be omitted introduction of the steam from outside when DME sufficiently contains water.

The reformed gas led into the methanation reactor 16 contacts the catalyst which fills the methanation reactor 16. Hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are converted into methane as in the above equations (2) and (4), so that the heating value of the reformed gas increases. This methanation reaction is carried out under the conditions of a temperature of 250 to 400 °C and a pressure of 0.49 to 7.84 MPa (5 to 80 kgf/cm²) in use of the catalyst known for methanation reaction, for example, a catalyst containing alumina, nickel and barium oxide, disclosed in Japanese Patent Publication No. 8810/1988. - -

Delete the paragraph on page 17 beginning at line 26 and ending at line 29 and substitute therefore the following amended paragraph:

- - Referring to Fig. 2, DME used for the carburant is sucked to a conduit 2p from a carburant storage with a pump 24P and then the DME is evaporated in an evaporator 20. Further, the evaporated DME is led into the conduit 2n through a valve 20V. Instead, it is possible to use LPG as the carburant. - -

On page 21, delete the last paragraph beginning at line 24 and ending in line 30 and substitute the following amended paragraph:

-- Reactor : The reactor is made of stainless steel, which has an adiabatic structure substantially shutting out the exchange of heat with the outside. Its internal diameter is 21.4 mm and its length is 1.5 m. In order to measure the temperature distribution of the catalyst layer with a thermocouple, a tube made of stainless steel is inserted into the center of the reactor. The tube has an external diameter of 3 mm and an internal diameter of 2 mm. The reactor as above described will be defined as an "Experimental Reactor A". --

Page 23, delete the last three paragraphs beginning at line 10 and ending at line 30 and substitute therefore the following amended paragraphs:

-- The second reforming reactor is an adiabatic reactor similar to the first reforming reactor. Its inlet pressure is 1.813 MPa (18.5 kg/cm²), as gauge pressure. A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1g] in Table 2, which is the gas indicated by [1f], adding DME at a rate of 200 kg-mol/h. Catalyst A of 200 cm³ is packed into Experimental Reactor A. W/F is 0.5 kg-catalyst•h/kg-DME. Previous to the reaction, the pretreatment of Catalyst A is carried out by a flow of hydrogen at a temperature 350 °C for eight hours under the atmospheric pressure.

As the result of the reaction under the condition of an inlet temperature of 285 °C of the reactor, the temperature of the exit of the catalyst layer rises to 545 °C, equal to that in the first reforming reactor. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that all of the DME reacts and the outlet gas has such a flow rate and composition as indicated by [1k] in Table 2.

③ The methanation reactor

A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1k] in Table 2 and that gas from the second reforming reactor is cooled to 280 °C and that the inlet pressure of the methanation reactor, which is an adiabatic reactor, is 1.666 MPa (17 kg/cm²), as gauge pressure. - -

Page 25, delete the paragraph beginning at line 10 and ending at line 22 and substitute therefore the following amended paragraph:

- - Reactor : A main body of the reactor is made of stainless steel. Its internal diameter is 53.1 mm and its height is 1.5 m. A sintered metal filter is welded to the lower part of the reactor in order to distribute a feed gas uniformly into the catalyst layer. An enlarged part is formed at the upper part of the reactor in order to prevent the powder of the catalyst from scattering out. Its internal diameter is 102.3 mm and its height is 70 cm. An internal cooler which is a coiled tube made of stainless steel, is arranged in the reactor, in order to cool the reactor by circulating hot water at a temperature of 140 °C. The total length of the tube is 7 m, and its external diameter is 3 mm and its internal diameter is 2 mm. A tube made of stainless steel is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with a thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm. - -

Page 27, delete the paragraph beginning at line 13 and ending at line 14 and substitute therefore the following amended paragraph:

- - Flow rate of source for town gas to be obtained under normal conditions is 350000 m³ a day. - -

Delete the paragraph beginning at line 30 on page 27, and ending at line 8 on page 28, and substitute therefore the following amended paragraph:

- - Reactor : Reaction tube is made of stainless steel. Its internal diameter is 21.4 mm and its length is 1.5 m. A jacket made of stainless steel is arranged at the outside of the reaction tubes. Its internal diameter is 81.1 mm. The reactor is so substantially isothermal that the reaction heat is eliminated by circulating hot water at a temperature 140 °C into the jacket. A stainless steel tube is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with a thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm. The reactor as above described will be defined as Experimental Reactor C. - -

Delete the first paragraph on page 30 beginning at line 1 and ending at line 5 and substitute therefore the following amended paragraph:

- - As the result of reaction without the pretreatment of the catalyst, the temperature of gas at the exit of the catalyst layer rises up to 350 °C. As the result of analysis of the composition of the outlet gas of the reactor, all of the DME reacts and it proves that the outlet gas has such a flow rate and composition as indicated by [3h] in Table 4. - -

Delete the paragraph beginning at line 19 on page 30 and ending at line 22 on page 30 and substitute therefore the following amended paragraph:

- - Catalyst of 150 cm³ is packed into Experimental Reactor C. Compositions of this catalyst contain nickel of 10 wt% in the form of NiO and barium of 3 wt% in the form of BaO, which is supported by an alumina carrier extruded with a diameter of 3 mm and a length of 8 mm. - -

Delete the paragraphs beginning at line 7 on page 31 and ending at line 24 on page 32 and substitute there the following amended paragraphs:

-- Effect of Invention

This invention is practiced as provided in the above description. Hence, this invention has such effects as described in the following description.

According to the method for producing town gas, as a first claim of invention, it is efficient from the view of transportation of feed stock since water is not produced on the reforming reaction of dimethyl ether, which is feed stock. Accordingly, extra heat energy corresponding to water is not needed when evaporating feed stock. Further, the facilities for desulfurization, for supply of hydrogen used for the desulfurization process and for recycling the hydrogen are unnecessary since a sulfur component is not contained in dimethyl ether. Furthermore, small or medium-sized businesses can carry out the method of this invention to produce and supply town gas or substitute natural gas alternatively for LNG since cryogenic storage facilities are unnecessary.

In the method for producing town gas, as a second claim of invention, there is suppression of excess temperature rise of the reaction system due to the heat of the reforming reactor of dimethyl ether and extra consumption of heat energy needed to heat the feed stock supplied into the reforming reactor, or to cool the gas reformed in the reforming reactor, since quantity of the coexisting steam is controlled within a proper range. Furthermore, the extra consumption of heat energy needed to heat the feed stock, or to cool the reformed gas, can be suppressed in the case wherein the quantity of steam is large.

In the method for producing town gas, as a third claim of invention, the reforming reaction of dimethyl ether can smoothly proceed and the deactivation of the catalyst can be

prevented since the temperature of the reaction system is controlled within a predetermined range.

In the method for producing town gas, as a fourth claim of invention, town gas can be produced with a reactor having simplified equipment since adiabatic fixed bed reactors are plurally and serially installed through cooling means between the reactors for the reforming reaction of dimethyl ether and dimethyl ether is supplied into the reactors so as to suppress the temperature rise with heat of the reaction.

In the method for producing town gas, as a fifth claim of invention, town gas can be produced with a single reactor since a fluidized bed reactor or a multi-tubular reactor, which can efficiently remove the heat of reaction, is used for reforming dimethyl ether, which is an exothermic reaction.

In the method for producing town gas, as a sixth claim of invention, the heating value per unit volume of the reformed gas can be increased since carbon dioxide, which is an incombustible gas, is removed from the reformed gas.

In the method for producing town gas, as a seventh claim of invention, the operation of the producing process of town gas can be stabilized since the proven method is adopted for the removal of carbon dioxide.

In the method for producing town gas, as an eighth claim of invention, the heating value of the reformed gas can be increased since hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are methanized and carbon dioxide is removed from the reformed gas.

In the method for producing town gas, as a ninth claim of invention, the heating value of town gas as a final product, can be adapted to a predetermined value controlling quantity of carburant to add in the reformed gas. - -

Delete the Abstract in entirety on page 35 and substitute therefore the following amended abstract:

- - ABSTRACT

It is an object of this invention to provide a method for producing town gas, in which a sulfur component is not contained in the feed stock, so desulfurization facilities are unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and which is suitable for small or medium-sized businesses to carry out. Dimethyl ether is used as feed stock. After evaporating dimethyl ether, the dimethyl ether is heated under the existence of steam within a heating furnace 33. The heated dimethyl ether is led into a tubular reforming reactor filled with catalyst for reforming. Dimethyl ether comes into contact with the catalyst within the reactor and reformed in gas containing carbon dioxide, carbon monoxide, hydrogen and mainly methane. Next, the reformed gas is led into a pressure-swinging adsorbing apparatus 37, so that carbon dioxide is separated from the reformed gas. Then the reformed gas is led into a methanation reactor 38, so that hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are methanized. Finally, the heating value of the reformed gas is controlled by adding carburant which is dimethyl ether so as to transform into tow gas. - -

In the claims:

Delete original claims 1 through 9 and substitute therefore the following new claims 10 through 21:

10. A method for producing town gas comprising the steps of;
 - (A) preparing dimethyl ether as feed stock;
 - (B) evaporating said dimethyl ether and;
 - (C) reforming said dimethyl ether with steam in the presence of catalyst

to produce reformed gas containing mainly methane.

11. A method for producing town gas according to claim 10, in which the quantity of said steam on reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether.

12. A method for producing town gas according to claim 10, in which the temperature for catalytic reforming of said dimethyl ether is within 200 °C to 600 °C.

13. A method for producing town gas according to claim 10, in which said dimethyl ether is supplied serially to adiabatic fixed bed reactors through cooling means installed between said reactors.

14. A method for producing town gas according to claim 10, in which said dimethyl ether is divided and a divided portion thereof is serially supplied to adiabatic fixed bed reactors, and simultaneously supplying the remaining portion of said divided dimethyl ether to at least a subsequent one of said reactors.

15. A method for producing town gas according to claim 10, in which said dimethyl ether is reformed with a reactor selected from the group consisting of a fluidized bed reactor and a multi-tubular reactor.

16. A method for producing town gas according to claim 10, in which carbon dioxide by-produced by said reforming of said dimethyl ether is removed from said reformed gas after reforming said dimethyl ether.

17. A method for producing town gas according to claim 16, in which said carbon dioxide is removed from said reformed gas by absorption by a solution selected from the group consisting of a aqueous alkanolamine solution and a heated aqueous potassium carbonate solution.

18. A method for producing town gas according to claim 16, in which said carbon dioxide is removed from said reformed gas by adsorption by a pressure swinging method.

19. A method for producing town gas according to claim 16, in which said carbon dioxide is removed from said reformed gas by selective separation by membrane.

20. A method for producing town gas according to claim 16, in which hydrogen, carbon monoxide and carbon dioxide, which are by-produced on said reforming process, are methanized.

21. A method for producing town gas according to claim 10, in which a portion of said dimethyl ether is added to said reformed gas as carburant.

REMARKS

This Amendment corrects grammatical errors in the specification and corrects indefinite language in the original claims. It is believed that the foregoing amendments will greatly facilitate examination.

A marked up version of the amended paragraphs of the specification and claims follows in the attached appendix.

Respectfully submitted,

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Patent
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Application No.: PCT/JP00/03048)
Filed: May 26, 1999)
For: METHOD OF PRODUCING)
TOWN GAS)

Pittsburgh, Pennsylvania

APPENDIX: MARKED UP VERSION OF AMENDED PARAGRAPHS

Paragraphs beginning at line 7 on page 1 and ending on line 29 of page 5:

-- Background Art

Recently, in the major cities, town gas is obtained by evaporating liquefied natural gas (LNG). However, to produce town gas from LNG requires the facilities for maintaining the received LNG at an extremely low temperature under -162°C and for evaporating the LNG to produce town gas. Accordingly, it is not suitable for small or medium-sized businesses to produce town gas from LNG. Further, it is [forecasted] forecast that LNG [becomes] will become scarce [in resources] as a resource in the near future. Accordingly, it is desired that town gas [is] be made from feed stock [except] other than LNG or, from substitute natural gas (SNG). [And so] Accordingly various methods for producing town gas have been proposed.

- ① Methods using hydrocarbons as feed stock;

There are methods for producing town gas from hydrocarbons, such as liquefied petroleum gas (LPG) and naphtha. Japanese Patent Publication No. 51134/1987 discloses a method for producing gas containing methane (CH_4) as a main component, hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO), by means of steam reforming of hydrocarbons of carbon number 2 to 14 with the catalyst containing nickel, cerium and alumina. And Japanese Patent Opening Gazette No. 144089/1980 discloses a method for producing gas containing methane as a main component, by means of steam reforming of heavier hydrocarbons with the catalyst containing ruthenium. Further, Japanese Patent Opening Gazette No. 17003/1987 discloses a method for producing gas containing methane as a main component, by means of steam reforming of desulfurized hydrocarbons with the catalyst containing ruthenium.

② Methods using alcohols as feed stock;

There are methods for producing town gas from alcohols, such as methanol (CH_3OH) or a mixture of methanol and water (H_2O). Japanese Patent Publication No. 24835/1982 discloses a method for producing fuel gas of higher heating value where a gas containing methane, hydrogen, carbon dioxide and carbon monoxide, is produced by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium, followed by methanation of [those] the produced hydrogen and carbon monoxide. And Japanese Patent Opening Gazette No. 156196/1987 discloses a method for producing methane by a single step by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium and lanthanum as essential components.

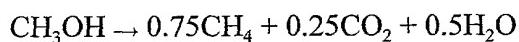
Further, Japanese Patent Opening Gazette No. 234499/1989 discloses a method for [efficiently] efficient evaporation of liquid phase methanol and water, which are heated by the heat of outlet gas of a reactor and are contacted directly with recycled gas. Japanese Patent Opening Gazette No. 304184/1989 discloses a method for separating carbon dioxide from gas

produced by the reaction between alcohol and steam, using liquid phase alcohol. Japanese Patent Opening Gazette No. 123737/1991 discloses a reactor of the type which recovers reaction heat to utilize this evaporation and preheat of feed stock.

And, we have not been able to find out the Prior [Arts] Art regarding a method for producing town gas from dimethyl ether as feed stock.

The above methods ① using hydrocarbons as feed stock require the facilities for desulfurization, supply of hydrogen used for the desulfurization, and hydrogen recycle, since such hydrocarbons as naphtha contain sulfur compounds. Further, sulfur in hydrogen sulfide produced on desulfurization process, is generally fixed as zinc sulfide. It cannot help in treating the zinc sulfide as industrial wastes since zinc sulfide is difficult to decompose and reuse, which causes environmental problems in the future.

The above methods ② use methanol as feed stock in many cases. Since methanol has been desulfurized in the course of production, desulfurization facilities are not newly required in these methods. In this respect, these methods are superior to the above methods using hydrocarbons as feed stock. However, producing town gas from methanol is carried out according to the following reaction equation, theoretically;



That is, 0.75 mol carbon element in CH₃OH is converted into CH₄, and 0.25 mol of that are converted into CO₂. At this time, 0.5 mol of H₂O (water corresponding to 28% of the weight of methanol) is also produced. In point of transportation of feed stock, it is not economical since potentially reproduced water, not being fuel, is transported. Further, on the production of town gas, it is needed to evaporate the water when evaporating methanol. Accordingly, energy is unnecessarily consumed. Furthermore, it requires liquefied petroleum gas as carburant to make the town gas.

Accordingly, it is an object of this invention to provide a method for producing town gas, in which a sulfur component is not contained in the feed stock, so desulfurization facilities are unnecessary, and cryogenic storage facilities are also unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and liquefied petroleum gas is unnecessary as carburant, and which is suitable for small or medium-sized businesses to carry out.

Disclosure of Invention

The above object can be solved by the method for producing town gas, [of claim 1] as a first claim of the present invention; using dimethyl ether (CH_3OCH_3 or $\text{C}_2\text{H}_6\text{O}$) as feed stock, and evaporating the dimethyl ether, and reforming the dimethyl ether catalytically under the existence of steam, and producing gas mainly containing methane [mainly].

The dimethyl ether used for feed stock can be crude dimethyl ether containing, alcohols which contain methanol as a main component, and/or water. Such a method for producing town gas is carried out according to the following reaction equation, theoretically:



Coexistent steam functions to suppress temperature rise of the reaction system.

It is evident from the above reaction equation that 0.75 mol of carbon element in 1 mol $\text{C}_2\text{H}_6\text{O}$ is converted into CH_4 , and 0.25 mol of that are converted into CO_2 , which is similar to the case using methanol as feed stock. However, this method using dimethyl ether is efficient and advantageous from the view of transportation, since H_2O is not reproduced. Further, heat energy is not unnecessarily consumed on the evaporation process of the feed stock.

In a method for producing town gas, [of claim 2 according to claim 1] as a second claim of invention, the quantity of the steam for catalytic reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether. Necessary [quantity] quantities of the steam is ordinarily obtained

by means of introduction into the reaction system from outside. However, in the case wherein the dimethyl ether contains water beyond some quantity, the steam to be introduced from the outside may be unnecessary. The quantity of the coexistent steam to suppress the temperature rise of the reaction system is reduced and the consumption of heat energy is reduced in the method for producing town gas according to [claim 2] the present invention.

In a method for producing town gas, [of claim 3 according to claim 1] as a third claim of invention, the temperature for the catalytic reforming of the dimethyl ether is within 200 °C to 600 °C, and preferably within 250 °C to 550 °C. Such a method prevents deactivation of the catalyst caused by excess temperature rise of the reaction system.

In a method for producing town gas, [of claim 4 according to claim 1] as a fourth claim of invention, dimethyl ether is supplied to serially installed adiabatic fixed bed reactors, under the existence of steam, by one of the following manners;

- ① Passing cooling means installed between the reactors, dimethyl ether is supplied serially to the reactors;
- ② A part of divided dimethyl ether is supplied to the reactors serially, and at the same time, the remaining part of the divided dimethyl ether is supplied to the subsequent reactors.

Such a method suppresses excess temperature rise of the reaction system caused by heat of the reforming reaction in the case of using an adiabatic fixed bed reactor.

In a method for producing town gas, [of claim 5 according to claim 1] as a fifth claim of invention, dimethyl ether is reformed with a fluidized bed reactor or a multi-tubular reactor which is in [a] the form of [the] a single stage or [the] plural stages. Such a method for producing town gas prevents excess temperature rise of the reaction system by simplified equipment.

In a method for producing town gas, [of claim 6 according to claim 1] as a sixth claim of invention, by-produced carbon dioxide is removed from the reformed gas of dimethyl ether. Such a method produces gas of higher heating value not containing incombustible gas.

In a method for producing town gas, [of claim 7 according to claim 6] as a seventh claim of invention, carbon dioxide is removed using any of the following manners;

- ① Absorption by aqueous alkanolamine solution or heated aqueous potassium carbonate solution;
- ② Adsorption by pressure swinging;
- ③ Selective separation by membrane.

Such a method [surely] positively removes carbon dioxide from the reformed gas.

In a method for producing town gas, [of claim 8 according to claim 1] as an eighth claim of invention, hydrogen, carbon monoxide and carbon dioxide, which are by-produced on the reforming process of dimethyl ether, are methanized either before or after removing carbon dioxide from the reformed gas. Such a method furthermore increases [furthermore] the heating value of the produced reformed gas.

In a method for producing town gas, [of claim 9 according to claim 1] as a ninth claim of invention, dimethyl ether used for feed stock is added to the produced reformed gas as carburant. Special facilities for storage or supply of carburant is unnecessary in contrast to such other [carburant] carburants as liquefied petroleum gas, and the heating value of product gas can be controlled so as to adjust to the standardization. - -

Paragraphs on page 6 beginning at line 13 and ending in line 25:

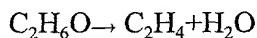
-- Conventionally, dimethyl ether is produced by dehydration of methanol which is produced in advance. However, in recent years, the dimethyl ether tends to be directly produced by the reaction between hydrogen and carbon monoxide as in the following equation;

$$4\text{H}_2 + 2\text{CO} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$$

In this reaction, CH_3OH is sometimes by-produced besides H_2O . In this invention, not only pure dimethyl ether but also crude dimethyl ether containing alcohols of which the main component is methanol, and/or water, can be used for feed stock. Since dimethyl ether does not contain sulfur components, similar to methanol, desulfurization facilities are unnecessary [on] for the production of the town gas. Further, since the boiling point of dimethyl ether is -25.1 °C, which is close to that of methanol, [the] cryogenic storage facilities as needed for LNG, [is] are unnecessary. --

Paragraphs beginning at line 26 on page 7 and ending at line 8 on page 9:

-- The reforming reaction of the equation (1) is highly exothermic. Hence, when the temperature of the reaction system rises excessively, the reforming reaction of the equation (1) [becomes] will not [to] proceed toward the right side due to chemical equilibrium. Besides, there is a possibility of the side reaction which produces ethylene (C_2H_4) as in the following equation;



Ethylene deposits resinous material on the surface of the catalyst and prevents the reforming reaction. Accordingly, it is desirable to control the reaction temperature within the above temperature range by cooling the reaction system adequately. In this invention, steam coexists

for reforming reaction of dimethyl ether. The principal purpose of coexistence of steam is to suppress the temperature rise of the reaction system.

However, the coexistence of the steam requires extra thermal energy for heating or cooling the steam, in the whole of the production process of the town gas. Accordingly, it is not economical that the quantity of the steam is beyond 10/1 mole ratio (steam/dimethyl ether)[. And] and the preferable quantity of the steam is under 10/1, and more preferably under a ratio of 5/1 [ratio]. However, it becomes difficult to suppress the temperature rise of the reaction system when the quantity of the steam is under a ratio of 0.5/1 [ratio]. Accordingly, a most preferable quantity of the steam is [the] within a ratio of 1/1-2/1 [ratio] in consideration of the steam quantity to be used and [easiness] the ease of temperature control of the reaction system.

As a reactor used for the reaction process of reforming dimethyl ether catalytically, there can be used an adiabatic fixed bed reactor which has no internal cooling means. In this case, special considerations are required for keeping the reaction temperature within the preferable range.

For example, dimethyl ether is supplied to a plurally and serially installed adiabatic fixed bed reactor filled with catalyst, under the existence of steam, according to the following [manners] procedures; ① passing cooling means installed between the reactors, dimethyl ether is serially supplied to the reactors, or ② dimethyl ether is divided into two or more parts, and a part of the dimethyl ether is serially supplied to the reactors, and at the same time, the [remains] remainder of [part of] the dimethyl ether is supplied to the subsequent reactors.

Besides, when a fluidized bed reactor or a multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system is sufficiently cooled down. It may be used in a single stage. The fluidized bed reactor has a perforated plate under a fluidized

layer of powdery catalyst. The powdery catalyst is fluidized by introduction of feed gas through the perforated plate and is cooled down by internal cooling means. The multi-tubular reactor has many reaction tubes filled with catalyst. The outside of the reaction tubes is formed as a jacket and is flowed with a medium for cooling the catalyst. In the case that the fluidized bed reactor or the multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system can be easily controlled with the coexistence of steam. - -

Paragraph beginning at line 17 on page 9 and ending at line 24 of page 9:

- - Both reactions are reversible and absorbent can be regenerated.

② Adsorption by pressure swinging;

CO₂ is adsorbed on silica gel, molecular sieve or active carbon under higher pressure and desorbed under [the] atmospheric or lower pressure.

③ Selective separation by membrane;

Only CO₂ can be separated selectively from the mixture of CH₄ and CO₂ by a membrane having a large permeability of CO₂, such as polyimide, cellulose ester, or polysulfon membranes. - -

Delete the first paragraph on page 12 beginning at line 1 and ending at line 10 and substitute therefore the following amended paragraph:

- - It is apparent from Table 1 that the latent heat of vaporization of dimethyl ether is smaller than that of methanol, and so the heat energy for vaporization of dimethyl ether is smaller than that of methanol. Further, in the theoretical value of the product of methane per unit volume of transported liquid, dimethyl ether is larger than methanol. In this respect, dimethyl ether is superior to methanol as feed stock to be transported. Furthermore, the heat of dimethyl ether on reforming is [larger] greater. Accordingly, [there can be more efficiently used] the heat

of the reforming reaction can be used more efficiently for vaporization and heating of dimethyl ether as feed stock. As above described, it is more beneficial to use dimethyl ether as feed stock of town gas. - -

Paragraphs beginning at line 9 on page 13 and ending at line 13 on page 14:

- -The reason that the reforming reaction of DME is divided into two, by supplying DME into the first and second reforming reactor 15A, 15B together with the steam, is to prevent depositing resinous materials on the surface of the catalyst in the reactors and deactivation of the catalyst due to sintering, besides the fact that the reforming reaction of DME shown by the above equation (1) [becomes] will not [to] proceed toward the right side in chemical equilibrium when the temperature of the reaction system rises excessively with heat of the reforming reaction, which is an exothermic reaction. In this respect, reforming reactors may be installed serially as three or more. Further, in the case that DME contains enough water [enough], a process flow which does not introduce the steam from outside, is applicable, omitting the water storage 14, the pump 14P and the conduits 1c, 1d from Fig. 1.

DME is supplied serially into the first and second reforming reactors 15A, 15B in the above. However, a part of the DME may be supplied serially into the first and second reforming reactors 15A, 15B, and at the same time, another part of the DME may be directly supplied into the second reforming reactor 15B.

Referring to Fig. 1, DME from the DME storage 11 is divided [into] in two at a downstream point of the heat exchanger 12a. A part of the divided DME is heated at a top portion of the heating furnace 13 through a conduit 1h and then is supplied into the second reforming reactor 15B through the conduit 1g together with the outlet gas of the first reforming reactor 15A.

According to such a [manner] procedure, it is possible to [more] better equalize the load distribution between the first and second reforming reactors 15A, 15B. Equalization of reaction temperature can be facilitated. Further, there can be omitted introduction of the steam from outside when DME sufficiently contains water [sufficiently].

The reformed gas led into the methanation reactor 16 contacts the catalyst which fills the methanation reactor 16. Hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are converted into methane as in the above equations (2) and (4), so that the heating value of the reformed gas increases. This methanation reaction is carried out under the conditions of a temperature of 250 to 400 °C and a pressure of 0.49 to 7.84 MPa (5 to 80 kgf/cm²) in use of the catalyst known for methanation reaction, for example, a catalyst containing alumina, nickel and barium oxide, disclosed in Japanese Patent Publication No. 8810/1988. - -

Paragraph on page 17 beginning at line 26 and ending at line 29:

- - Referring to Fig. 2, DME used for the carburant is sucked to a conduit 2p from a carburant storage with a pump 24P and then the DME is evaporated in an evaporator 20. Further, the evaporated DME is led into the conduit 2n through a valve 20V. [Insteads] Instead, it is possible to use LPG as the carburant. - -

On page 21, and ending in line 30:

- - Reactor : The reactor is made of stainless steel, which has an adiabatic structure substantially shutting out the exchange of heat with the outside. Its internal diameter is 21.4 mm and its length is 1.5 m. In order to measure the temperature distribution of the catalyst layer with a thermocouple, a tube made of stainless steel is inserted into the center of the reactor. The tube

has an external diameter of 3 mm and an internal diameter of 2 mm. The reactor as above described will be defined as an "Experimental Reactor A". - -

Page 23, beginning at line 10 and ending at line 30:

- - The second reforming reactor is an adiabatic reactor [similarly] similar to the first reforming reactor. Its inlet pressure is 1.813 MPa (18.5 kg/cm²), as gauge pressure. A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1g] in Table 2, which is the gas indicated by [1f], adding DME at a rate of 200 kg-mol/h. Catalyst A of 200 cm³ is packed into Experimental Reactor A. W/F is 0.5 kg-catalyst•h/kg-DME. Previous to the reaction, the pretreatment of Catalyst A is carried out by a flow of hydrogen at a temperature 350 °C for eight hours under the atmospheric pressure.

As the result of the reaction under the condition of an inlet temperature of 285 °C of the reactor, the temperature of the exit of the catalyst layer rises to 545 °C, equal to that in the first reforming reactor. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that all of the DME [react] reacts and the outlet gas has such a flow rate and composition as indicated by [1k] in Table 2.

③ The methanation reactor

A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1k] in Table 2 and that gas from the second reforming reactor is cooled to 280 °C and that the inlet pressure of the methanation reactor, which is an adiabatic reactor, is 1.666 MPa (17 kg/cm²), as gauge pressure. - -

Page 25, beginning at line 10 and ending at line 22:

-- Reactor : A main body of the reactor is made of stainless steel. Its internal diameter is 53.1 mm and its height is 1.5 m. A sintered metal filter is welded to the lower part of the reactor in order to distribute a feed gas uniformly into the catalyst layer. An enlarged part is formed at the upper part of the reactor in order to prevent [from] the powder of the catalyst [to scatter] from scattering out. Its internal diameter is 102.3 mm and its height is 70 cm. An internal cooler which is a coiled tube made of stainless steel, is arranged in the reactor, in order to cool the reactor by circulating hot water at a temperature of 140 °C. [Its] The total length of the tube is 7 m, and its external diameter is 3 mm and its internal diameter is 2 mm. A tube made of stainless steel is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with a thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm. --

Page 27, beginning at line 13 and ending at line 14:

-- Flow rate of source for town gas to be obtained under [the] normal [condition] conditions is 350000 m³ a day. --

Delete the paragraph beginning at line 30 on page 27, and ending at line 8 on page 28, and substitute therefore the following amended paragraph:

-- Reactor : Reaction tube is made of stainless steel. Its internal diameter is 21.4 mm and its length is 1.5 m. A jacket made of stainless steel is arranged at the outside of the reaction tubes. Its internal diameter is 81.1 mm. The reactor is so substantially isothermal that the reaction heat is eliminated by circulating hot water at a temperature 140 °C into the jacket. A stainless steel tube is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with a thermocouple. The external diameter of the tube is 3 mm

and its internal diameter is 2 mm. The reactor as above described will be defined as Experimental Reactor C. --

Paragraph on page 30 beginning at line 1 and ending at line 5:

-- As the result of reaction without the pretreatment of the catalyst, the temperature of gas at the exit of the catalyst layer rises up to 350 °C. As the result of analysis of the composition of the outlet gas of the reactor, all of the DME [react] reacts and it proves that the outlet gas has such a flow rate and composition as indicated by [3h] in Table 4. --

Paragraph beginning at line 19 on page 30 and ending at line 22 on page 30:

-- Catalyst of 150 cm³ is packed into Experimental Reactor C. Compositions of this catalyst [contains] contain nickel of 10 wt% in the form of NiO and barium of 3 wt% in the form of BaO, which is supported by an alumina carrier extruded with a diameter of 3 mm and a length of 8 mm. --

Paragraphs beginning at line 7 on page 31 and ending at line 24 on page 32:

-- Effect of Invention

This invention is [practised] practiced as provided in the above description. Hence, this invention has such [effect] effects as described in the following description.

According to the method for producing town gas, [of claim 1] as a first claim of invention, it is efficient from the view of transportation of feed stock since water is not produced on the reforming reaction of dimethyl ether, which is feed stock. Accordingly, extra heat energy corresponding to water is not needed when evaporating feed stock. Further, the facilities for desulfurization, for supply of hydrogen used for the desulfurization process and for recycling the

hydrogen are unnecessary since a sulfur component is not contained in dimethyl ether. Furthermore, small or medium-sized businesses can [be carried] carry out [by] the method of this invention to produce and supply town gas or substitute natural gas alternatively for LNG since cryogenic storage facilities are unnecessary.

In the method for producing town gas, [of claim 2] as a second claim of invention, [there can be suppressed the] there is suppression of excess temperature rise of the reaction system due to the heat of the reforming reactor of dimethyl ether and [the] extra consumption of heat energy needed to heat the feed stock supplied into the reforming reactor, or to cool the gas reformed in the reforming reactor, since quantity of the coexisting steam is controlled within a proper range. Furthermore, [there can be suppressed] the extra consumption of heat energy needed to heat the feed stock, or to cool the reformed gas, can be suppressed in the case [that] wherein the quantity of [the] steam is large.

In the method for producing town gas, [of claim 3] as a third claim of invention, [there can be smoothly proceeded] the reforming reaction of dimethyl ether can smoothly proceed and [there can be prevented] the deactivation of the catalyst can be prevented since the temperature of the reaction system is controlled within a predetermined range.

In the method for producing town gas, [of claim 4] as a fourth claim of invention, [there can be produced] town gas can be produced with a reactor having simplified equipment since adiabatic fixed bed reactors are plurally and serially installed through cooling means between the reactors for the reforming reaction of dimethyl ether and dimethyl ether is supplied into the reactors so as to suppress the temperature rise with heat of the reaction.

In the method for producing town gas, [of claim 5] as a fifth claim of invention, [there can be produced] town gas can be produced with a single reactor since a fluidized bed

reactor or a multi-tubular reactor, which can efficiently remove the heat of reaction, is used for reforming dimethyl ether, which is an exothermic reaction.

In the method for producing town gas, [of claim 6] as a sixth claim of invention, [there can be increased] the heating value per unit volume of the reformed gas can be increased since carbon dioxide, which is an incombustible gas, is removed from the reformed gas.

In the method for producing town gas, [of claim 7] as a seventh claim of invention, [there can be stabilized] the operation of the producing process of town gas can be stabilized since the proven method is adopted for the removal of carbon dioxide.

In the method for producing town gas, [of claim 8] as an eighth claim of invention, [there can be increased] the heating value of the reformed gas can be increased since hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are methanized [besides] and carbon dioxide is removed from the reformed gas.

In the method for producing town gas, [of claim 9] as a ninth claim of invention, the heating value of town gas as a final product, can be adapted to a predetermined value controlling quantity of carburant to add in the reformed gas. --

Abstract on page 35:

-- ABSTRACT

It is an object of this invention to provide a method for producing town gas, in which a sulfur component is not contained in the feed stock, so desulfurization facilities are unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and which is suitable for small or medium-sized businesses [can] to carry out. [As a means to solve. dimethyl] Dimethyl ether is used as feed stock. After evaporating dimethyl ether, the dimethyl ether is heated under the existence of steam within a

heating furnace 33. The heated dimethyl ether is led into a tubular reforming reactor filled with catalyst for reforming. Dimethyl ether comes into contact with the catalyst within the reactor and reformed in gas containing carbon dioxide, carbon monoxide, hydrogen and mainly methane [mainly]. Next, the reformed gas is led into a pressure-swinging [adsobing] adsorbing apparatus 37, so that carbon dioxide is separated from the reformed gas. [And then] Then the reformed gas is led into a methanation reactor 38, so that hydrogen, carbon monoxide and [carabon] carbon dioxide, which are contained in the reformed gas, are methanized. Finally, the heating value of the reformed gas is controlled by adding carburant which is dimethyl ether so as to [change] transform into tow gas. --

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DESCRIPTION

Method for producing town gas

Technical Field

This invention relates to a method for producing town gas, and more particularly to a method for producing town gas containing methane as a main component using dimethyl ether as feed stock.

Background Art

Recently, in the major cities, town gas is obtained by evaporating liquefied natural gas (LNG). However, to produce town gas from LNG requires the facilities for maintaining the received LNG at extremely low temperature under -162 °C and for evaporating the LNG to produce town gas. Accordingly, it is not suitable for small or medium-sized businesses to produce town gas from LNG. Further, it is forecasted that LNG becomes scarce in resources in the near future. Accordingly, it is desired that town gas is made from feed stock except LNG or, from substitute natural gas (SNG). And so various methods for producing town gas have been proposed.

① Methods using hydrocarbons as feed stock;

There are methods for producing town gas from hydrocarbons, such as liquefied petroleum gas (LPG) and naphtha. Japanese Patent Publication No. 51134/1987 discloses a method for producing gas containing methane (CH_4) as a main component, hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO), by means of steam reforming of hydrocarbons of carbon number 2 to 14 with the catalyst containing nickel, cerium and alumina. And Japanese Patent Opening Gazette No.144089/1980 discloses a method for producing gas containing methane as a main component, by means of steam reforming of heavier hydrocarbons with the catalyst containing ruthenium. Further, Japanese Patent Opening Gazette No.17003/1987 discloses a method for producing gas containing methane as a main component, by means of steam reforming of

desulfurized hydrocarbons with the catalyst containing ruthenium.

② Methods using alcohols as feed stock;

There are methods for producing town gas from alcohols, such as methanol (CH_3OH) or mixture of methanol and water (H_2O). Japanese Patent Publication No.24835/1982 discloses a method for producing fuel gas of higher heating value where a gas containing methane, hydrogen, carbon dioxide and carbon monoxide, is produced by contacting methanol or mixture of methanol and water with the catalyst containing ruthenium, followed by methanation of those produced hydrogen and carbon monoxide. And Japanese Patent Opening Gazette No.156196/1987 discloses a method for producing methane by a single step by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium and lanthanum as essential components.

Further, Japanese Patent Opening Gazette No.234499/1989 discloses a method for efficiently evaporation of liquid phase methanol and water, which are heated by the heat of outlet gas of a reactor and are contacted directly with recycled gas. Japanese Patent Opening Gazette No. 304184/1989 discloses a method for separating carbon dioxide from gas produced by the reaction between alcohol and steam, using liquid phase alcohol. Japanese Patent Opening Gazette No.123737/1991 discloses a reactor of the type which recovers reaction heat to utilize this evaporation and preheat of feed stock.

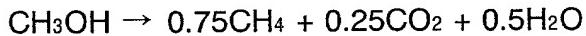
And, we have not been able to find out the Prior Arts regarding a method for producing town gas from dimethyl ether as feed stock.

The above methods ① using hydrocarbons as feed stock require the facilities for desulfurization, supply of hydrogen used for the desulfurization, and hydrogen recycle, since such hydrocarbons as naphtha contain sulfur compounds. Further, sulfur in hydrogen sulfide produced on desulfurization process, is generally fixed as zinc sulfide. It cannot help treating the zinc sulfide as industrial wastes since zinc sulfide is difficult to decompose and reuse, which causes environmental problems in the future.

The above methods ② use methanol as feed stock in many cases. Since

methanol has been desulfurized in the course of production, desulfurization facilities are not newly required in these methods. In this respect, these methods are superior to the above methods using hydrocarbons as feed stock.

However, producing town gas from methanol is carried out according to the following reaction equation, theoretically;



That is, 0.75 mol carbon element in CH_3OH is converted into CH_4 , and 0.25 mol of that are converted into CO_2 . At this time, 0.5 mol of H_2O (water corresponding to 28% of the weight of methanol) is also produced. In point of transportation of feed stock, it is not economical since potentially reproduced water, not being fuel, is transported. Further, on the production of town gas, it is needed to evaporate the water when evaporating methanol. Accordingly, energy is unnecessarily consumed. Furthermore, it requires liquefied petroleum gas as carburant to make the town gas.

Accordingly, it is an object of this invention to provide a method for producing town gas, in which sulfur component is not contained in feed stock, so desulfurization facilities are unnecessary, and cryogenic storage facilities are also unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and liquefied petroleum gas is unnecessary as carburant, and which is suitable for small or medium-sized businesses to carry out.

Disclosure of Invention

The above object can be solved by the method for producing town gas, of claim 1; using dimethyl ether (CH_3OCH_3 or $\text{C}_2\text{H}_6\text{O}$) as feed stock, and evaporating the dimethyl ether, and reforming the dimethyl ether catalytically under the existence of steam, and producing gas containing methane mainly.

The dimethyl ether used for feed stock can be crude dimethyl ether containing, alcohols which contain methanol as main component, and/or water. Such a method for producing town gas is carried out according to the following reaction equation, theoretically:



Coexistent steam functions to suppress temperature rise of reaction system.

It is evident from the above reaction equation that 0.75 mol of carbon element in 1 mol $\text{C}_2\text{H}_6\text{O}$ is converted into CH_4 , and 0.25 mol of that are converted into CO_2 , which is similar to the case using methanol as feed stock. However, this method using dimethyl ether is efficient and advantageous from view of transportation, since H_2O is not reproduced. Further, heat energy is not unnecessarily consumed on the evaporation process of the feed stock.

In a method for producing town gas, of claim 2 according to claim 1, quantity of the steam for catalytic reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether. Necessary quantity of the steam is ordinarily obtained by means of introduction into the reaction system from outside. However, in the case the dimethyl ether contains water beyond some quantity, the steam to be introduced from the outside may be unnecessary. The quantity of the coexistent steam to suppress the temperature rise of the reaction system is reduced and the consumption of heat energy is reduced in the method for producing town gas according to claim 2.

In a method for producing town gas, of claim 3 according to claim 1, the temperature for the catalytic reforming of the dimethyl ether is within 200 °C to 600 °C, and preferably within 250 °C to 550 °C. Such a method prevents deactivation of the catalyst caused by excess temperature rise of the reaction system.

In a method for producing town gas, of claim 4 according to claim 1, dimethyl ether is supplied to serially installed adiabatic fixed bed reactors, under the existence of steam, by one of the following manners;

- ① Passing cooling means installed between the reactors, dimethyl ether is supplied serially to the reactors;
- ② A part of divided dimethyl ether is supplied to the reactors serially, and at the same time, the remaining part of the divided dimethyl ether is supplied to the

subsequent reactors.

Such a method suppresses excess temperature rise of reaction system caused by heat of the reforming reaction in the case of using adiabatic fixed bed reactor.

In a method for producing town gas, of claim 5 according to claim 1, dimethyl ether is reformed with fluidized bed reactor or multi-tubular reactor which is in a form of the single stage or the plural stages. Such a method for producing town gas prevents excess temperature rise of reaction system by simplified equipment.

In a method for producing town gas, of claim 6 according to claim 1, by-produced carbon dioxide is removed from the reformed gas of dimethyl ether. Such a method produces gas of higher heating value not containing incombustible gas.

In a method for producing town gas, of claim 7 according to claim 6, carbon dioxide is removed using any of the following manners;

- ① Absorption by aqueous alkanolamine solution or heated aqueous potassium carbonate solution;
- ② Adsorption by pressure swinging;
- ③ Selective separation by membrane.

Such a method surely removes carbon dioxide from the reformed gas.

In a method for producing town gas, of claim 8 according to claim 1, hydrogen, carbon monoxide and carbon dioxide, which are by-produced on reforming process of dimethyl ether, are methanized either before or after removing carbon dioxide from the reformed gas. Such a method increases furthermore the heating value of the produced reformed gas.

In a method for producing town gas, of claim 9 according to claim 1, dimethyl ether used for feed stock is added to the produced reformed gas as carburant. Special facilities for storage or supply of carburant is unnecessary in contrast to such other carburant as liquefied petroleum gas, and heating value of product gas can be controlled so as to adjust to the standardization.

Brief Description of Drawings

Fig.1 is the first product flow scheme, as one example which is applied to the embodiment of this invention.

Fig.2 is the second product flow scheme, as another example which is applied to the embodiment of this invention.

Fig.3 is the third product flow scheme, as a further example which is applied to the embodiment of this invention.

Best Mode for Carrying Out the Invention

As above described, a method for producing town gas according to this invention comprises the steps of; using dimethyl ether as feed stock; evaporating the dimethyl ether and; reforming the dimethyl ether with steam in the presence of catalyst to produce reformed gas containing mainly methane .

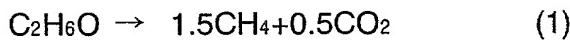
Conventionally, dimethyl ether is produced by dehydration of methanol which is produced in advance. However, in recent years, the dimethyl ether tends to be directly produced by the reaction between hydrogen and carbon monoxide as following equation;



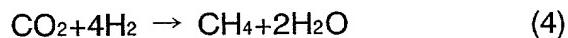
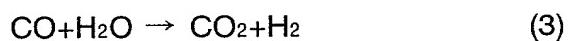
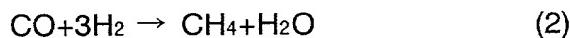
In this reaction, CH_3OH is sometimes by-produced besides H_2O . In this invention, not only pure dimethyl ether but also crude dimethyl ether containing alcohols of which main component is methanol, and/or water, can be used for feed stock. Since dimethyl ether does not contain sulfur components, similar to methanol, desulfurization facilities are unnecessary on the production of the town gas. Further, since the boiling point of dimethyl ether is -25.1 °C , which is close to that of methanol, the cryogenic storage facilities as needed for LNG, is unnecessary.

Any methods can be adopted to reform dimethyl ether catalytically under the existence of steam. The gas containing mainly methane is produced with the reaction shown in equation (1), by means of reforming the dimethyl ether catalytically within 200 °C to 600 °C , and preferably within 250 °C to 550 °C of

temperature, using well-known catalysts for reforming hydrocarbon, such as the catalyst containing ruthenium (Ru) disclosed in Japanese Patent Opening Gazette No.17003/1987, or the catalyst containing nickel (Ni), cerium (Ce) and alumina (Al_2O_3) disclosed in Japanese Patent Publication No.51134/1987;



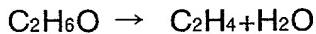
In practice, H_2 and CO are also produced besides CH_4 and CO_2 produced with the reaction equation (1). Simultaneously, the following equation (2), (3) and (4) proceed;



Accordingly, when dimethyl ether is reformed catalytically, the reformed gas contains H_2 , CO, CO_2 , H_2O , and mainly CH_4 . Compositions of the reforming gas vary with the reaction temperature, catalysts and so on. The compositions of the reformed gas besides H_2O , are about 50~70% CH_4 , 20~25% CO_2 , 10~30% H_2 and 0~3% CO.

In the case that the catalyst containing nickel is used for the reforming or methanation, generally the reduction treatment of the catalyst with hydrogen is required in advance. Accordingly, the hydrogen supply facilities are needed similarly to the case of producing the town gas from LPG. However, they can be simplified because they are not used for the desulfurization in contrast to the case of LPG. And also hydrogen recycling facilities are unnecessary. In recent years, some commercially supplied catalysts are stabilized by partial reduction. When such catalyst is used, the hydrogen supply sources are not always necessary.

The reforming reaction of the equation (1) is highly exothermic. Hence, when the temperature of the reaction system rises excessively, the reforming reaction of the equation (1) becomes not to proceed toward right side due to chemical equilibrium. Besides, there is a possibility of the side reaction which produces ethylene (C_2H_4) as the following equation;



Ethylene deposits resinous material on the surface of the catalyst and prevents the reforming reaction. Accordingly, it is desirable to control the reaction temperature within the above temperature range by cooling the reaction system adequately. In this invention, steam coexists for reforming reaction of dimethyl ether. The principal purpose of coexistence of steam is to suppress the temperature rise of the reaction system.

However, the coexistence of the steam requires extra thermal energy for heating or cooling the steam, in the whole of the production process of the town gas. Accordingly, it is not economical that quantity of the steam is beyond 10/1 mole ratio (steam/dimethyl ether). And preferable quantity of the steam is under 10/1, and more preferably under 5/1 ratio. However, it becomes difficult to suppress the temperature rise of the reaction system when quantity of the steam is under 0.5/1 ratio. Accordingly, most preferable quantity of the steam is the within 1/1~2/1 ratio in consideration of the steam quantity to be used and easiness of temperature control of the reaction system.

As a reactor used for the reaction process of reforming dimethyl ether catalytically, there can be used an adiabatic fixed bed reactor which has no internal cooling means. In this case, special considerations are required for keeping the reaction temperature within the preferable range.

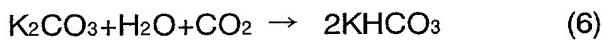
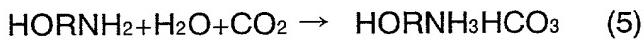
For example, dimethyl ether is supplied to plurally and serially installed adiabatic fixed bed reactor filled with catalyst, under the existence of steam, according to the following manners; ① passing cooling means installed between the reactors, dimethyl ether is serially supplied to the reactors, or ② dimethyl ether is divided into two or more, and a part of dimethyl ether is serially supplied to the reactors, and at the same time, the remains of part of dimethyl ether is supplied to the subsequent reactors.

Besides, when a fluidized bed reactor or a multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system is sufficiently cooled down. It may be used in single stage. The fluidized bed

reactor has a perforated plate under a fluidized layer of powdery catalyst. The powdery catalyst is fluidized by introduction of feed gas through the perforated plate and is cooled down by internal cooling means. The multi-tubular reactor has many reaction tubes filled with catalyst. The outside of the reaction tubes is formed as a jacket and is flowed with medium for cooling the catalyst. In the case that the fluidized bed reactor or the multi-tubular reactor is used for reforming dimethyl ether, the temperature of reaction system can be easily controlled with the coexistence of steam.

After reforming dimethyl ether, incombustible carbon dioxide is removed from the reformed gas. Any method for removing carbon dioxide can be adopted. In this invention, one of the following proven methods is preferably adopted.

- ① Absorption by aqueous alkanolamine solution (HORNH_2) or heated aqueous potassium carbonate solution (K_2CO_3);



Both reactions are reversible and absorbent can be regenerated.

- ② Adsorption by pressure swinging;

CO_2 is adsorbed on silica gel, molecular sieve or active carbon under higher pressure and desorbed under the atmospheric or lower pressure.

- ③ Selective separation by membrane;

Only CO_2 can be separated selectively from the mixture of CH_4 and CO_2 by membrane having a large permeability of CO_2 , such as polyimide, cellulose ester, polysulfon membranes.

Besides the removal of carbon dioxide, preferably, methanations of carbon monoxide, hydrogen and carbon dioxide, which are by-produced on the reforming process of dimethyl ether, are carried out to increase the heating value. The methanations of CO , CO_2 and H_2 are carried out with the catalyst, preferably containing alumina, nickel and barium oxide (BaO) as disclosed in Japanese Patent Publication No.8810/1988, besides the catalyst containing

nickel and cobalt (Co) as disclosed in Japanese Patent Publication No.24835/1982. And the methanation may be carried out either before or after eliminating carbon dioxide.

Further, dimethyl ether used as feed stock may be added as carburant, to the reformed gas. In the case that the heating value of the town gas is standardized, the heating value of the reformed gas is adjusted to the standardized heating value by adding some quantity of the carburant. Dimethyl ether used for carburant may be at the gaseous state or at the liquid state. In the case that dimethyl ether is at the liquid state, it is added to the reformed gas through vaporizer.

Table 1 shows various characteristics of the town gas produced from dimethyl ether, comparing with the town gas produced from methanol.

(Table 1) Comparison of various characteristics on producing of fuel gas.

feed stock	dimethyl ether	$\text{CH}_3\text{OH} \rightarrow$ $0.75\text{CH}_4 + 0.25\text{CO}_2 + 0.5\text{H}_2\text{O}$	methanol
theoretical reaction equation	$\text{C}_2\text{H}_6\text{O} \rightarrow 1.5\text{CH}_4 + 0.5\text{CO}_2$		
heat of reaction (kcal/mol-feed stock)	30.8		17.7
latent heat of vaporization (kcal/mol-feed stock)	5.14		8.43
liquid density (kmol/m ³ -transport liquid)	668		790
storage density (kmol/m ³ -transport liquid)	14.5		24.7
amount of theoretical formation of methane (Nm ³ methane/m ³ -transport liquid)	488		415

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It is apparent from Table 1 that the latent heat of vaporization of dimethyl ether is smaller than that of methanol, and so the heat energy for vaporization of dimethyl ether is smaller than that of methanol. Further, in the theoretical value of the product of methane per unit volume of transported liquid, dimethyl ether is larger than methanol. In this respect, dimethyl ether is superior to methanol as feed stock to be transported. Furthermore, the heat of dimethyl ether on reforming is larger. Accordingly, there can be more efficiently used the heat of the reforming reaction for vaporization and heating of dimethyl ether as feed stock. As above described, it is more beneficial to use dimethyl ether as feed stock of town gas.

Next, a method for producing town gas according to embodiments of this invention will be described with reference to the drawings. Hereafter, "DME" will mean the abbreviation of "dimethyl ether".

(First embodiment of this invention)

Fig.1 shows a product flow scheme of town gas according to this embodiment. Two adiabatic fixed bed reactors are serially installed for reforming reaction. In Fig.1, DME, sucked with a pump 11P from a DME storage 11 to a conduit 1a, is evaporated in a heat exchanger 12a and the DME is supplied into a bottom portion of a heating furnace 13 through a conduit 1b.

On the other hand, water, sucked with a pump 14P from a water storage 14, is supplied into the heating furnace 13 through a conduit 1c and the water is steamed up at a portion 1d of the conduit 1c which passes the heating furnace 13. The steam is led into the conduit 1b and then the steam and the DME are joined there. That is, DME is supplied into the bottom portion of the heating furnace 13 together with the steam and heated therein. Then, the DME is supplied through a conduit 1e into a first reforming reactor 15A which is an adiabatic fixed bed reactor. The first reforming reactor 15A does not have any internal cooling means. Further, the DME contacts with catalyst which fills the reactor 15A, and then the DME is reformed with reaction as the above equations (1), (2), (3) and (4).

Gas which is led out from the first reforming reactor 15A through a conduit 1f is intermediately cooled in a cooler 15AR and then the gas is supplied through a conduit 1g into a second reforming reactor 15B which is an adiabatic fixed bed reactor. In the second reforming reactor 15B, the gas is reformed catalytically like the first reforming reactor 15A, additionally. Reformed gas which is led out from the second reforming reactor 15B into a conduit 1k, is cooled in a cooler 15BR installed on the way of the conduit 1k, and then the reformed gas is supplied to a methanation reactor 16.

The reason that the reforming reaction of DME is divided into two, by supplying DME into the first and second reforming reactor 15A, 15B together with the steam, is to prevent depositing resinous materials on the surface of the catalyst in the reactors and deactivation of the catalyst due to sintering, besides the fact that the reforming reaction of DME shown by the above equation (1) becomes not to proceed toward right side in chemical equilibrium when the temperature of the reaction system rises excessively with heat of the reforming reaction which is exothermic reaction. In this respect, reforming reactors may be installed serially three or more. Further, in the case that DME contains water enough, a process flow which does not introduce the steam from outside, is applicable, omitting the water storage 14, the pump 14P and the conduits 1c,1d from Fig.1.

DME is supplied serially into the first and second reforming reactors 15A,15B in the above. However, a part of DME may be supplied serially into the first and second reforming reactors 15A,15B, and at the same time, another part of DME may be directly supplied into the second reforming reactor 15B.

Referring to Fig.1, DME from the DME storage 11 is divided into two at a downstream point of the heat exchanger 12a. A part of the divided DME is heated at a top of the heating furnace 13 through a conduit 1h and then is supplied into the second reforming reactor 15B through the conduit 1g together with the outlet gas of the first reforming reactor 15A.

According to such a manner, it is possible to more equalize the load

distribution between the first and second reforming reactors 15A, 15B. Equalization of reaction temperature can be facilitated. Further, there can be omitted introduction of the steam from outside when DME contains water sufficiently.

The reformed gas led into the methanation reactor 16 contacts the catalyst which fills the methanation reactor 16. Hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are converted into methane as the above equations (2) and (4), so that the heating value of the reformed gas increases. This methanation reaction is carried out under the conditions of a temperature of 250 to 400 °C and a pressure of 0.49 to 7.84 MPa (5 to 80 kgf/cm²) in use of the catalyst known for methanation reaction, for example, a catalyst containing alumina, nickel and barium oxide, disclosed in Japanese Patent Publication No.8810/1988.

The methanation reactor 16 is shown as an adiabatic fixed bed reactor in Fig.1. Instead, it may be a fluidized bed reactor or a multi-tubular reactor.

The reformed gas from the methanation reactor 16 is led into a conduit 1m and exchanges heats with the feed stock DME in the heat exchanger 12a. And then the reformed gas is led into a heat exchanger 12b through a conduit 1n and is cooled therein. Further, the reformed gas is led into a condensing tank 17A through a conduit 1j and condensed water is separated. The condensed water is discharged from a bottom portion of the condensing tank 17A. Furthermore, the reformed gas is cooled in a cooler 17BR located at a portion of a conduit 1p which connects the condensing tank 17A and a condensing tank 17B, and condensed water is separated in the condensing tank 17B. The condensed water is discharged from a bottom portion of the condensing tank 17B.

The reformed gas from which moisture is separated, is led into a bottom portion of a carbon dioxide absorbing tower 18 through a conduit 1q. Aqueous alkanolamine solution is led into a top portion of the absorbing tower 18 through a conduit 1y and is poured towards the bottom portion of the absorbing tower 18.

On the other hand, the reformed gas introduced into the tower 18 rises toward the top portion of the absorbing tower 18. Accordingly, there occurs the countercurrent gas-liquid contact between the reformed gas and the aqueous alkanolamine solution in the absorbing tower 18. Therefore, the carbon dioxide in the reformed gas is absorbed as expressed in the above equation (5).

Accordingly, the reformed gas from which carbon dioxide is removed, is obtained from the top portion of the absorbing tower 18 through a conduit 1r, as the source of town gas. The heating value of the source gas is controlled by means of addition of DME as carburant on the way of the extraction of the source gas so as to be used for town gas.

The DME as carburant is led into an evaporator 10 through a conduit 1z which branches off from the conduit 1a and the DME is evaporated therein. The evaporated DME is added to the conduit 1r through a valve 10V.

In the case that the crude DME containing methanol, any other alcohols or water, is used for feed stock, it cannot be used as the carburant. Accordingly, it is necessary to add high-purity DME or any other carburants, separately.

The aqueous alkanolamine solution absorbing carbon dioxide at high concentration, is led into a conduit 1s from the bottom portion of the carbon dioxide absorbing tower 18. And then the solution is led into a top portion of an aqueous alkanolamine regenerating tower 19 through a heat exchanger 12c and the conduit 1s.

Liquid extracted from a bottom portion of the regenerating tower 19 is led into the heat exchanger 12b through a conduit 1u and is heated therein. And then the heated liquid is returned to the bottom portion of the regenerating tower 19 through a conduit 1v.

The aqueous alkanolamine solution is heated by the above means in the regenerating tower 19. Hence, the carbon dioxide absorbed in the aqueous alkanolamine solution is evolved and so the aqueous alkanolamine solution is regenerated.

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The evolved carbon dioxide is discharged from the top portion of the regenerating tower 19 through a conduit 1w. On the other hand, the regenerated aqueous alkanolamine solution is discharged from the bottom portion of the regenerating tower 19 with a pump 19P. Then, the solution is led into a cooler 19R through a conduit 1x and the heat exchanger 12c, and is cooled therein. Further, the solution is returned to the top of the carbon dioxide absorbing tower 18 through the conduit 1y.

In the above description, the removal of carbon dioxide in the reformed gas is carried out with absorption by aqueous alkanolamine solution. However, any other methods can be adopted to remove the carbon dioxide.

(Second embodiment of this invention)

Fig.2 shows a product flow scheme of town gas according to this embodiment. In this embodiment, crude DME containing water is used for the feed stock of town gas and a fluidized bed reactor is adopted as a reforming reactor.

Referring to Fig.2, crude DME, sucked with a pump 21P from a crude DME storage 21 to a conduit 2a, is led into a heat exchanger 22a and is evaporated therein. And then the evaporated crude DME is led into a heating furnace 23 and is heated therein. The heated crude DME is led into a bottom portion of a fluidized bed reactor 25 through a conduit 2c. The fluidized bed reactor 25 has internal cooling means. In the fluidized bed reactor 25, the crude DME comes into contact with powdery catalysts, blowing up and fluidizing the powdery catalysts. Hence, the crude DME is reformed with the reactions, with the above equations (1),(2),(3) and (4). The components of catalysts, and the conditions of the temperature and pressure on the reforming reaction, are similar to those for the first embodiment of this invention.

The reformed gas is led into a heat exchanger 22b through a conduit 2d and is cooled therein. And then, the reformed gas is led into the heat exchanger 22a through a conduit 2e and is cooled therein. Further, the reformed gas is led into a cooler 26R through a conduit 2f and is cooled therein.

Furthermore, the reformed gas is led into a condensing tank 26 and condensed water is separated therein. The condensed water is discharged from a bottom portion of the condensing tank 26.

The reformed gas in the condensing tank 26 is led into a selective membrane-separating apparatus 27 through a conduit 2g. In this apparatus, the reformed gas comes into contact with a selective separating membrane, which is made of polyimide, and the carbon dioxide is selectively separated from the reformed gas. That is, there is a filmy module composed of a bundle of a large number of hollow fibers, in the apparatus 27. These hollow fibers are about 1 mm in outside diameter. The reformed gas is supplied to the outside of the hollow fibers and only the carbon dioxide in the reformed gas permeates the wall of the hollow fibers. Hence, the carbon dioxide is led into the inside of the hollow fibers.

The separated carbon dioxide is discharged from the apparatus 27 through a conduit 2h. The reformed gas from which the carbon dioxide is removed, is led into a cooler 28R through conduits 2j,2k and a heat exchanger 22b and then the reformed gas is cooled therein. Further, the cooled reformed gas is led into a condensing tank 28 and condensed water separated in the condensing tank 28 is discharged from a bottom portion of the tank 28.

The reformed gas from which the condensed water is separated, is extracted through a conduit 2n as a source of town gas. The heating value of the source gas is controlled by addition of pure DME as carburant on the way of the extraction of the source gas so as to be used for town gas. That is, it is not possible to use crude DME as the carburant since the crude DME contains water.

Referring to Fig.2, DME used for the carburant is sucked to a conduit 2p from a carburant storage with a pump 24P and then the DME is evaporated in an evaporator 20. Further, the evaporated DME is led into the conduit 2n through a valve 20V. Insteads, it is possible to use LPG as the carburant.

In the case that the fluidized bed reactor 25 is used for a reforming reactor,

it is relatively easy to remove the reaction heat on the reforming reaction. While the method for producing town gas, which uses the crude DME as feed stock and which does not use the steam, has been described in this embodiment. It is apparently possible to use the steam to cool the reforming reaction system. Further, a method for removing the carbon dioxide is not restricted to the above mentioned. Furthermore, it is able to include the process of the methanation reaction between hydrogen, carbon monoxide and carbon dioxide in the reformed gas.

(Third embodiment of this invention)

Fig.3 shows a third product flow scheme according to this embodiment. In this embodiment, multi-tubular reactors are used as the reforming reactors.

Referring to Fig.3, DME, sucked with a pump 31P from a DME storage 31 into a conduit 3a, is led into a heat exchanger 32a and is evaporated therein. And then the evaporated DME is led into a bottom portion of a heating furnace 33 through a conduit 3b and is heated therein. Further, the heated DME is led into many reaction tubes 35T arranged within a multi-tubular reactor 35.

On the other hand, water sucked with a pump 34P from a water storage 34 is led into the heating furnace 33 through a conduit 3c. The water is steamed up at a part 3d of the conduit 3c which goes through the heating furnace 33. And then the steam is led into a jacket 35J of the multi-tubular reactor 35 through a conduit 3f.

The multi-tubular reactor 35 consists of many reaction tubes 35T filled with catalysts, and the jacket 35J positioned at the outsides of those reaction tubes 35T.

Hot water or steam within the jacket 35J cools the reaction tubes 35T and is discharged through a conduit 3g. And then the hot water or the steam is led into the conduit 3b in which DME flows.

That is, the DME within the conduit 3b is led into the bottom portion of the heating furnace 33 together with the steam and is heated therein. And then the DME is led into the multi-tubular reactor 35 through the conduit 3e and contacts

with the catalysts within the reaction tubes 35T. In consequence, the DME is reformed in accordance with the above reaction equations (1),(2),(3) and (4).

The catalysts with which the reaction tubes 35T are filled, and a temperature and pressure of the reforming reaction are similar to those for the first embodiment.

The reformed gas extracted through a conduit 3h is led into a conduit 3j through a heat exchanger 32b. And then the reformed gas is led into a conduit 3k through the heat exchanger 32a. Further, the reformed gas is cooled in a cooler 36R and is led into a condensing tank 36. Condensed water is separated from the reformed gas within the condensing tank 36 and is discharged from a bottom portion of the tank 36. The reformed gas from which the condensed water is separated, is led into a pressure-swinging adsorbing apparatus 37 through a conduit 3n and carbon dioxide in the reformed gas is removed by adsorption therein.

That is, the apparatus 37 is filled with molecular sieves as adsorbent. Plural adsorbing towers, adsorbing carbon dioxide under a pressure of 0.49 to 7.84MPa (5 to 80 kg/cm²) and evolving the adsorbed carbon dioxide under atmospheric pressure or a reduced pressure, are arranged within the apparatus 37. These adsorbing towers are by turns used. The evolved carbon dioxide is discharged through a conduit 3p and the reformed gas from which carbon dioxide is removed, is extracted through a conduit 3q.

The reformed gas from which carbon dioxide is removed, is led into the heat exchanger 32b through the conduit 3q and is pre-heated therein. And then the reformed gas is led into a methanation reactor 38 which is a multi-tubular reactor, through a conduit 3r. The inside of reaction tubes 38T arranged within the methanation reactor 38, are filled with catalysts for methanation reaction and the inside of a jacket 38J is flowed with hot water or steam for coolant. The hot water or the steam circulates through the jacket 38J by internal cooling means 38C.

That is, the reformed gas from which carbon dioxide is removed, contacts

with the catalysts in the reaction tubes 38T, and hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are converted into methane with the above reaction equations (2) and (4), and so the heating value of the reformed gas increases. The catalysts used for the methanation reaction, and a temperature and pressure of the methanation reaction are similar to those for the above first embodiment.

In this embodiment, the methanations of hydrogen and carbon monoxide are carried out after removing carbon dioxide. It is different from the above first embodiment which carries out the methanations before removing carbon dioxide. Both "after" and "before" may be adopted in principle. However, in the case that the concentration of carbon dioxide is higher than that of hydrogen and carbon monoxide, the methanations of hydrogen and carbon monoxide can be efficiently carried out when removal of carbon dioxide is carried out before the methanations. On the contrary, in the case that the concentrations of hydrogen and carbon monoxide are higher than that of carbon dioxide, methanizing hydrogen and carbon monoxide before removing carbon dioxide, can decrease the losses of hydrogen and carbon monoxide on the removing process of carbon dioxide and can methanize also carbon dioxide at the same time.

The reformed gas extracted from the methanation reactor 38 is led into a cooler 39R through a conduit 3s and is cooled therein. And then the reformed gas is led into a condensing tank 39 and condensed water is separated from the reformed gas. The condensed water is discharged from a bottom portion of the condensing tank 39. The reformed gas from which the condensed water is separated, is extracted as a source for town gas, through a conduit 3u. The heating value of the reformed gas is controlled so as to be town gas, by addition of DME as a carburant on the way of the conduit 3u. That is, the DME is led into an evaporator 30 from the DME storage 31, through a conduit 3z which branches off from the conduit 3a. And then the DME is evaporated in the evaporator 30 and is led into the conduit 3u in which the reformed gas flows, through a valve 30V.

Next, process simulations and experimental reactions according to the above first, second and third embodiments will be described.

(Example 1)

First, there will be described an example of producing town gas by supplying DME at a rate of 400 kg-mol/h (18400 kg/h), according to the first embodiment with reference to Fig.1. In this example, the steam is introduced at a rate of 1000 kg-mol/h (18000 kg/h) and the DME is introduced divisionally to the first and second reforming reactors at a rate of 200 kg-mol/h (9200 kg/h), respectively.

① The first reforming reactor

The first reforming reactor is an adiabatic reactor. Its inlet pressure is 1.96 MPa (20 kg/cm²), as gauge pressure, and its inlet temperature is 300 °C.

A reaction experiment is carried out under the following conditions, using a feed gas which has such compositions as indicated by [1e] in Table 2;

Catalyst : Compositions of the catalyst are nickel of 60 wt% in the form of NiO, cerium of 25 wt% in the form of CeO₂ and alumina of 15 wt%. The catalyst is formed from powdery state into the pellets having 3 mm in diameter and 3 mm in length (hereafter the catalyst formed under the above conditions, is named "Catalyst A"). The amount of the catalyst is 200 cm³.

W/F : W/F is 0.5 kg-catalyst · h / kg-DME.

W/F represents the weight of the catalyst (kg) per supply ratio of unit weight of DME or crude DME (kg/h). The same definition is used in the following examples.

Reactor : The reactor is made of stainless steel, which has an adiabatic structure substantially shutting out the exchange of heat with the outside. Its internal diameter is 21.4 mm and its length is 1.5 m. In order to measure the temperature distribution of catalyst layer with thermocouple, a tube made of stainless steel is inserted into the center of the reactor. The tube has an external diameter 3 mm and an internal diameter 2 mm. The reactor as above described will be defined as an "Experimental Reactor A".

(Table 2) Example of material balance according to first embodiment.

	1 e	1 f	1 g	1 k	1 m	1 r
inlet gas of first reforming reactor	outlet gas of first reforming reactor	inlet gas of second reforming reactor	outlet gas of second reforming reactor	outlet gas of methanation reactor	source gas for town gas	
[kg/mol/h]	[kg·mol/h]	[mol%]	[kg·mol/h]	[mol%]	[kg·mol/h]	[mol%]
DME	200.0	0.0	200.0	11.7	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0	0.0
CH ₄	0.0	246.8	16.4	246.8	14.5	532.3
H ₂	0.0	203.6	13.5	203.6	11.9	250.8
CO	0.0	9.3	0.6	9.3	0.5	20.1
CO ₂	0.0	143.9	9.6	143.9	8.4	247.6
H ₂ O	1000.0	902.9	59.9	902.9	52.9	884.7
TOTAL	1200.0	1506.4	100.0	1706.4	100.0	1935.5
temperature (°C)	300	545	285	545	280*/400	40
pressure (kg/cm ² G)	20.0		18.5		17.0**	14.0

* inlet temperature
** inlet pressure

Previous to the reaction, the pretreatment of Catalyst A is carried out by a flow of hydrogen at a temperature of 350 °C for eight hours under the atmospheric pressure. As the result of the reaction under the condition of an inlet temperature 300 °C of the reactor, the temperature of the exit of the catalyst layer rises to 545 °C. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that all of the DME reacts and the outlet gas has such flow rate and composition as indicated by [1f] in Table 2.

② The second reforming reactor

The second reforming reactor is an adiabatic reactor similarly to the first reforming reactor. Its inlet pressure is 1.813 MPa (18.5 kg/cm²), as gauge pressure. A reaction experiment is carried out under the condition that a feed gas has such flow rate and composition as indicated by [1g] in Table 2, which is the gas indicated by [1f], adding DME at a rate of 200 kg-mol/h. Catalyst A of 200 cm³ is packed into Experimental Reactor A. W/F is 0.5 kg-catalyst · h/kg-DME. Previous to the reaction, the pretreatment of Catalyst A is carried out by a flow of hydrogen at a temperature 350 °C for eight hours under the atmospheric pressure.

As the result of the reaction under the condition of an inlet temperature of 285 °C of the reactor, the temperature of the exit of the catalyst layer rises to 545 °C equal to that in the first reforming reactor. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that all of the DME react and the outlet gas has such flow rate and composition as indicated by [1k] in Table 2.

③ The methanation reactor

A reaction experiment is carried out under the condition that a feed gas has such flow rate and composition as indicated by [1k] in Table 2 and that gas from the second reforming reactor is cooled to 280 °C and that the inlet pressure of the methanation reactor which is an adiabatic reactor is 1.666 MPa (17 kg/cm²), as gauge pressure.

Catalyst of 50 cm³ is packed into Experimental Reactor A. Compositions of this catalyst are nickel of 35 wt% in the form of NiO, magnesium of 12 wt% in the form of MgO and alumina of 53 wt%. The catalyst is formed from powdery state into the pellet having 3 mm in diameter and 3 mm in length.

Feed gas supply rate under the normal condition (m³/h) per unit volume of catalyst layer (m³) is 15000 h⁻¹.

Previous to the reaction, the pretreatment of the catalyst is carried out by a flow of hydrogen at a temperature 280 °C for eight hours under the atmospheric pressure. As the result of the reaction under the condition of an inlet temperature 280 °C of the reactor, the temperature of the exit of the catalyst layer rises to 400 °C. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that the outlet gas has such flow rate and composition as indicated by [1m] in Table 2.

④ Removal of carbon dioxide

A process simulation, cooling the outlet gas of the methanation reactor and removing carbon dioxide with the absorbing tower in which the number of the theoretical plates is fifteen, is carried out. Mono ethanolamine solution is used for absorbent. Ratio of removed carbon dioxide in the reformed gas is 91.2 % under the condition that the temperature of the top of the absorbing tower is 40 °C and that the pressure in the tower is 1.372 MPa (14 kg/cm²), as gauge pressure. It proves that source for town gas has such flow rate and composition as indicated by [1r] in Table 2.

Flow rate of the source for town gas to be obtained under the normal condition is 360000 m³ a day.

(Example 2)

Next, there will be described an example of producing town gas by supplying crude DME, containing DME of 65 wt% and methanol of 9 wt% and water of 26 wt%, at a rate of 28200 kg/h, according to the second embodiment with reference to Fig.2. In this example, rate of DME contained in the feed gas is 400 kg-mol/h (18400 kg/h) and no steam is introduced from the outside.

① Reforming reactor

The reforming reactor is a fluidized bed reactor having internal cooling means. Its inlet pressure is 2.94 MPa (30 kg/cm²), as gauge pressure, and its inlet temperature is 300 °C. A reaction experiment, using a feed gas having such composition as indicated by [2c] in Table 3, is carried out under the following condition ;

Catalyst : Catalyst containing ruthenium of 2 wt%, is supported by alumina powder having a mean particle size 80 micrometers. The amount of the packed catalyst is 1500 cm³.

Reactor : A main body of the reactor is made of stainless steel. Its internal diameter is 53.1 mm and its height is 1.5 m. A sintered metal filter is welded to the lower part of the reactor in order to distribute a feed gas uniformly into the catalyst layer. An enlarged part is formed at the upper part of the reactor in order to prevent from the powder of the catalyst to scatter out. Its internal diameter is 102.3 mm and its height is 70 cm. An internal cooler which is a coiled tube made of stainless steel, is arranged in the reactor, in order to cool the reactor by circulating hot water at a temperature of 140 °C. Its total length of the tube is 7 m, and its external diameter is 3 mm and its internal diameter is 2 mm. A tube made of stainless steel is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm.

W/F : W/F is 2.0 kg-catalyst · h / kg-crude DME.

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(Table 3) Example of material balance according to second embodiment.

2 c		2 d		2 n	
inlet gas of reforming reactor		outlet gas of reforming reactor		source gas for town gas	
[kg·mol/h]	[mol%]	[kg·mol/h]	[mol%]	[kg·mol/h]	[mol%]
DME	400.0	45.5	0.0	0.0	0.0
CH ₃ OH	80.0	9.1	0.0	0.0	0.0
CH ₄	0.0	0.0	657.1	49.6	0.0
H ₂	0.0	0.0	11.5	0.9	635.9
CO	0.0	0.6	0.2	0.0	98.3
CO ₂	0.0	0.0	222.7	16.8	0.0
H ₂ O	400.0	45.5	434.4	32.8	11.1
TOTAL	880.0	100.0	1325.9	100.00	100.0
temperature (°C)	300	330		647.0	100.0
pressure (kg/cm ² G)	30.0			40 25.0	

As the result of the reaction without the pretreatment of the catalyst, the temperature of all of the catalyst layer is uniformly 330 °C. As the result of analysis of the composition of the outlet gas of the reactor, DME and methanol react and it proves that the outlet gas has such flow rate and composition as indicated by [2d] in Table 3.

① Removal of carbon dioxide

A process simulation of the removal of carbon dioxide with the hollow fiber-membrane made of polyimide, is carried out under the condition that the outlet gas of the reforming reactor is cooled down to 40 °C and that the pressure of the outlet gas is 2.45 MPa (25 kg/cm²), as gauge pressure. In result, it proves that source gas for town gas has such flow rate and composition as indicated by [2n] in Table 3, is obtained.

Flow rate of source for town gas to be obtained under the normal condition is 350000 m³ a day.

(Example 3)

Next, there will be described an example for producing town gas by supplying DME at a rate of 400 kg-mol/h (18400 kg/h) according to the third embodiment with reference to Fig.3. In this example, a rate of 600 kg-mol/h (10800 kg/h) of steam is introduced.

① Reforming reactor

The reforming reactor is a single-tubular reactor. The inlet pressure of the reactor is 1.47 MPa (15 kg/cm²), as gauge pressure, and its inlet temperature is 300 °C. A reaction experiment is carried out, using a gas having such composition as indicated by [3e] in Table 4, under the following condition.

Catalyst : Catalyst containing ruthenium of 2 wt%, is supported by alumina extruded with a diameter 3 mm and a length 8 m. The amount of the catalyst is 200 cm³.

W/F : W/F is 1.5 kg-catalyst · h / kg-DME.

Reactor : Reaction tube is made of stainless steel. Its internal diameter

is 21.4 mm and its length is 1.5 m. A jacket made of stainless steel is arranged at the outside of the reaction tubes. Its internal diameter is 81.1 mm. The reactor is so substantially isothermal that the reaction heat is eliminated by circulating hot water at a temperature 140 °C into the jacket. A stainless steel tube is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm. The reactor as above described will be defined as Experimental Reactor C.

(Table 4) Example of material balance according to third embodiment

	3 e inlet gas of reforming reactor	3 h outlet gas of reforming reactor	3 q outlet gas of PSA	3 s outlet gas of methanation reactor	3 u source gas for town gas
[kg · mol/h]	[mol%]	[kg · mol/h]	[mol%]	[kg · mol/h]	[mol%]
DME	400.0	40.0	0.0	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0
CH ₄	0.0	0.0	593.5	42.0	569.4
H ₂	0.0	0.0	25.4	1.8	24.2
CO	0.0	0.0	0.4	0.0	0.4
CO ₂	0.0	0.0	206.0	14.6	21.2
H ₂ O	600.0	60.0	587.5	41.6	0.0
TOTAL	1000.0	100.0	1412.9	100.0	609.7
temperatuer (°C)	300	350	40	300*/300	40
pressure (kg/cm ² G)	15.0		13.0	10**	9.0

* inlet temperature

** inlet pressure

As the result of reaction without the pretreatment of the catalyst, the temperature of gas at the exit of the catalyst layer rises up to 350 °C. As the result of analysis of the composition of the outlet gas of the reactor, all of DME react and it proves that the outlet gas has such flow rate and composition as indicated by [3h] in Table 4.

② Removal of carbon dioxide

A process simulation of the removal of carbon dioxide with pressure swinging adsorbing (PSA) method, is carried out under the condition that the outlet gas of the reforming reactor is cooled down to 40 °C and that the pressure in the pressure swinging adsorbing apparatus is 1.274 MPa (13 kg/cm²), as gauge pressure. As the result, it proves that source for town gas has such flow rate and composition as indicated by [3q] in Table 4.

③ Methanation reactor

A reaction experiment is carried out under the condition that a feed gas has such composition as indicated by [3q] in Table 4, and that gas from the pressure swinging adsorbing apparatus is heated up to 300 °C and that the inlet pressure of methanation reactor which is a single-tubular reactor, is 0.98 MPa (10 kg/cm²), as gauge pressure.

Catalyst of 150 cm³ is packed into Experimental Reactor C. Compositions of this catalyst contains nickel of 10 wt% in the form of NiO and barium of 3 wt% in the form of BaO, which supported by alumina carrier extruded with a diameter 3 mm and a length 8 mm.

Feed gas supply rate under the atmospheric condition (m³/h) per unit volume of catalyst layer (m³) is 5000 per hour.

Previous to the reaction, the pretreatment of the catalyst is carried out by a flow of hydrogen at a temperature 300 °C for eight hours under the atmospheric pressure. As the result of the reaction under the condition of an inlet temperature 300 °C of the reactor, the temperature of the catalyst layer is 300 °C.

As the result of analysis of the compositions of the outlet gas of the

reactor, it proves that the outlet gas has such flow rate and composition as indicated by [3s] in Table 4.

And it proves that source for town gas has such composition as indicated by [3u] in Table 4, by cooling the outlet gas of the methanation reactor to 40 °C and that flow rate of source gas to be obtained under the normal condition is 320000 m³ a day.

Effect of Invention

This invention is practised as the above description. Hence, this invention has such effect as following description.

According to the method for producing town gas, of claim 1, it is efficient from view of transportation of feed stock since water is not produced on reforming reaction of dimethyl ether which is feed stock. Accordingly, extra heat energy corresponding to water is not needed when evaporating feed stock. Further, the facilities for desulfurization, for supply of hydrogen used for the desulfurization process and for recycling the hydrogen are unnecessary since sulfur component is not contained in dimethyl ether. Furthermore, small or medium-sized businesses can be carried out by the method of this invention to produce and supply town gas or substitute natural gas alternatively for LNG since cryogenic storage facilities are unnecessary.

In the method for producing town gas, of claim 2, there can be suppressed the excess temperature rise of the reaction system due to the heat of the reforming reactor of dimethyl ether and the extra consumption of heat energy needed to heat the feed stock supplied into the reforming reactor, or to cool the gas reformed in the reforming reactor, since quantity of the coexisting steam is controlled within a proper range. Furthermore, there can be suppressed the extra consumption of heat energy needed to heat the feed stock, or to cool the reformed gas, in the case that quantity of the steam is large.

In the method for producing town gas, of claim 3, there can be smoothly proceeded the reforming reaction of dimethyl ether and there can be prevented

the deactivation of the catalyst since the temperature of reaction system is controlled within a predetermined range.

In the method for producing town gas, of claim 4, there can be produced town gas with reactor having simplified equipment since adiabatic fixed bed reactors are plurally and serially installed through cooling means between the reactors for reforming reaction of dimethyl ether and dimethyl ether is supplied into the reactors so as to suppress the temperature rise with heat of the reaction.

In the method for producing town gas, of claim 5, there can be produced town gas with a single reactor since a fluidized bed reactor or a multi-tubular reactor, which can efficiently remove the heat of reaction, is used for reforming dimethyl ether, which is an exothermic reaction.

In the method for producing town gas, of claim 6, there can be increased the heating value per unit volume of the reformed gas since carbon dioxide which is an incombustible gas, is removed from the reformed gas.

In the method for producing town gas, of claim 7, there can be stabilized the operation of the producing process of town gas since proven method is adopted for the removal of carbon dioxide.

In the method for producing town gas, of claim 8, there can be increased the heating value of the reformed gas since hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are methanized besides carbon dioxide is removed form the reformed gas.

In the method for producing town gas, of claim 9, the heating value of town gas as final product, can be adapted to a predetermined value controlling quantity of carburant to add in the reformed gas.

CLAIMS

1. A method for producing town gas comprising the steps of;
 - (A) preparing dimethyl ether as feed stock;
 - (B) evaporating said dimethyl ether and;
 - (C) reforming said dimethyl ether with steam in the presence of catalyst to produce reformed gas containing mainly methane.
2. A method for producing town gas according to claim 1, in which quantity of said steam on reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether.
3. A method for producing town gas according to claim 1, in which temperature for catalytic reforming of said dimethyl ether is within 200 °C to 600 °C.
4. A method for producing town gas according to claim 1, in which said dimethyl ether is supplied to serially installed adiabatic fixed bed reactors by one of the following manners;
 - ① Passing cooling means installed between said reactors, said dimethyl ether is supplied serially to said reactors; and
 - ② A part of divided dimethyl ether is supplied to said reactors serially, and at the same time, the remaining part of said divided dimethyl ether is supplied to subsequent reactor or reactors.
5. A method for producing town gas according to claim 1, in which said dimethyl ether is reformed with a fluidized bed reactor or a multi-tubular reactor.
6. A method for producing town gas according to claim 1, in which carbon dioxide by-produced on reforming process of said dimethyl ether is removed from said reformed gas after reforming said dimethyl ether.
7. A method for producing town gas according to claim 6, in which said carbon dioxide is removed from said reformed gas by using one of the following manners;
 - ① Absorption by aqueous alkanolamine solution or heated aqueous potassium carbonate solution;

- ② Adsorption by pressure swinging method;
- ③ Selective separation by membrane.

8. A method for producing town gas according to claim 6, in which hydrogen, carbon monoxide and carbon dioxide, which are by-produced on said reforming process, are methanized either before or after removing said carbon dioxide.

9. A method for producing town gas according to claim 1, in which a part of said dimethyl ether is added to said reformed gas as carburant.

FIG. 1

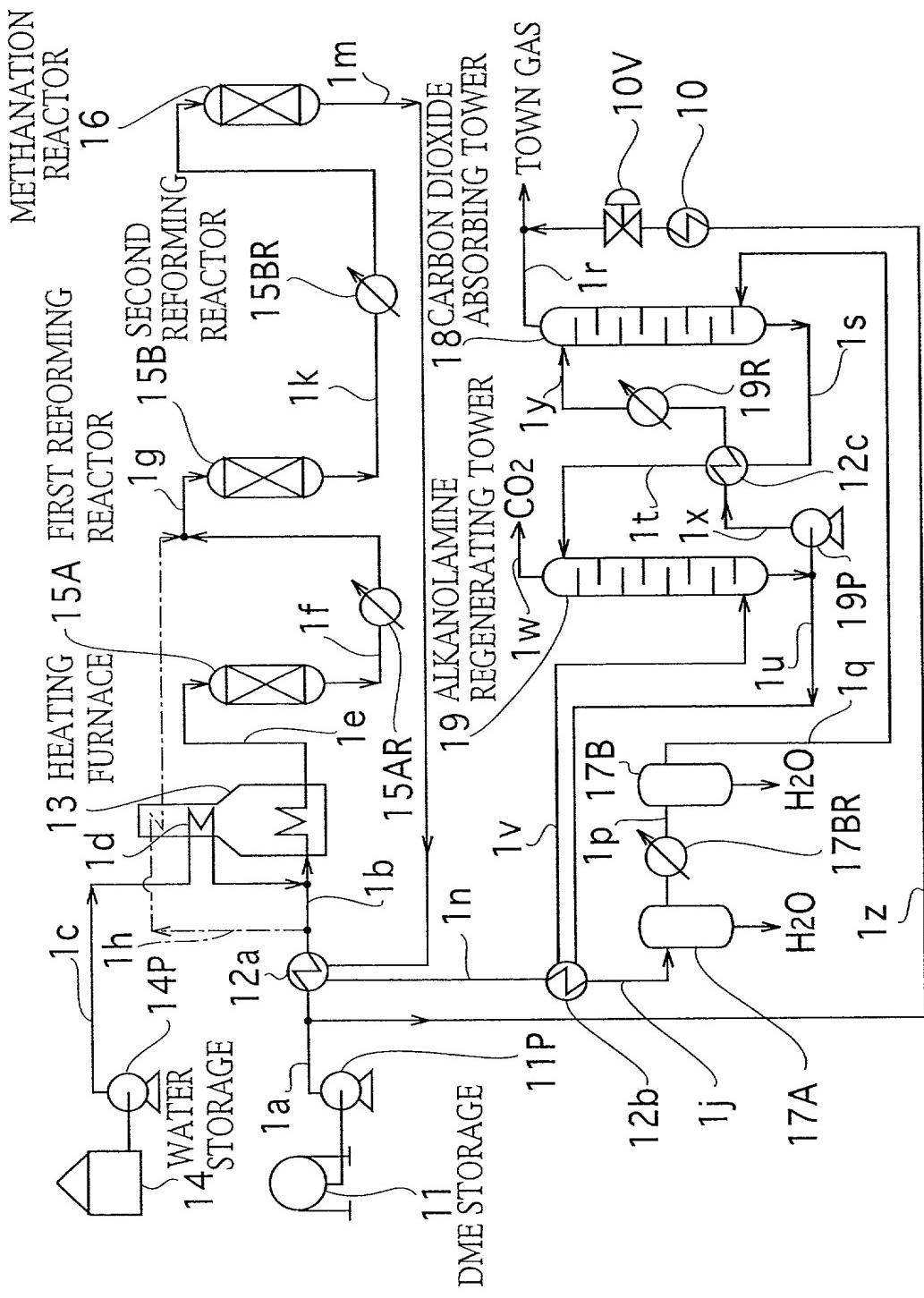
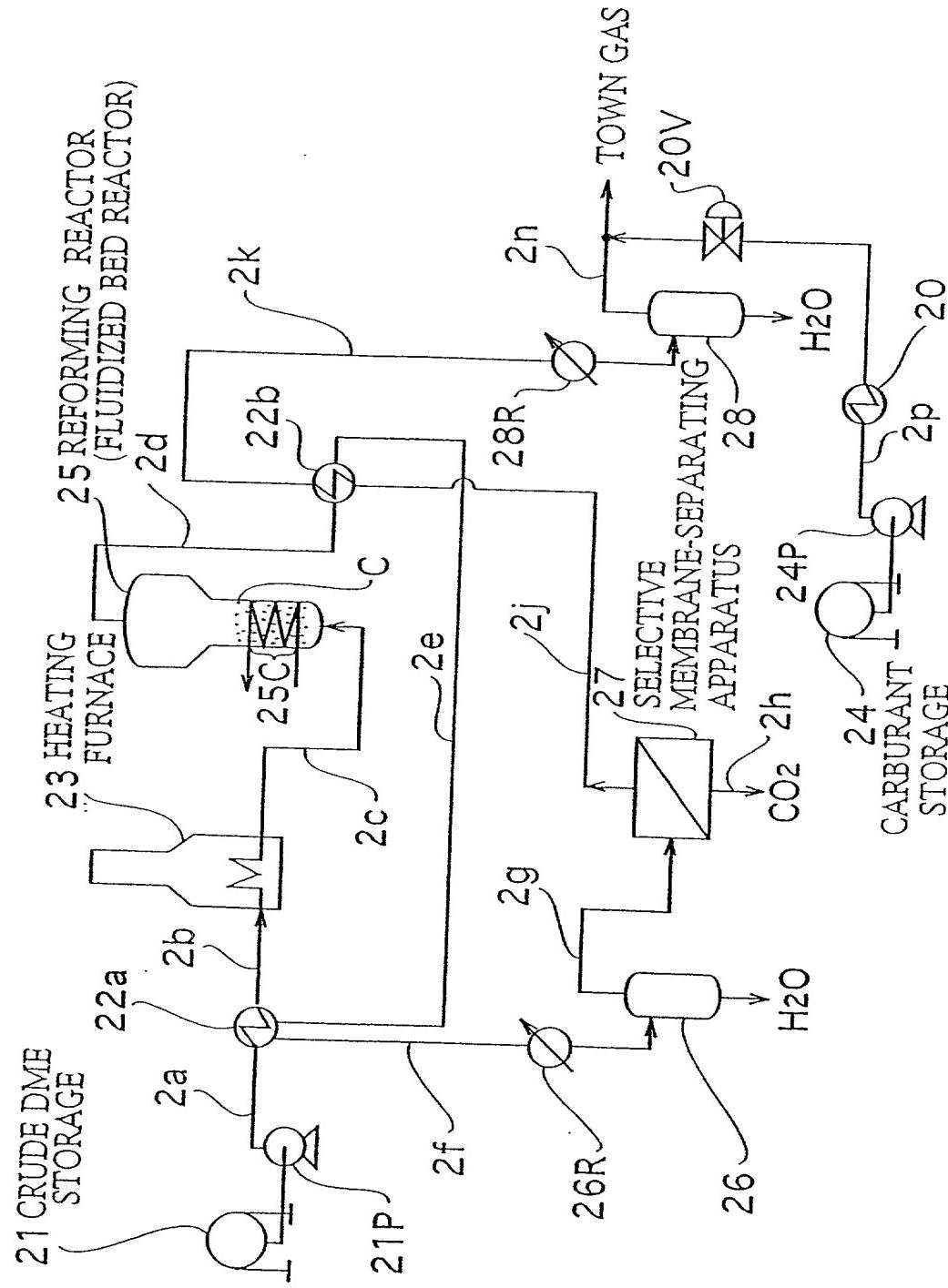
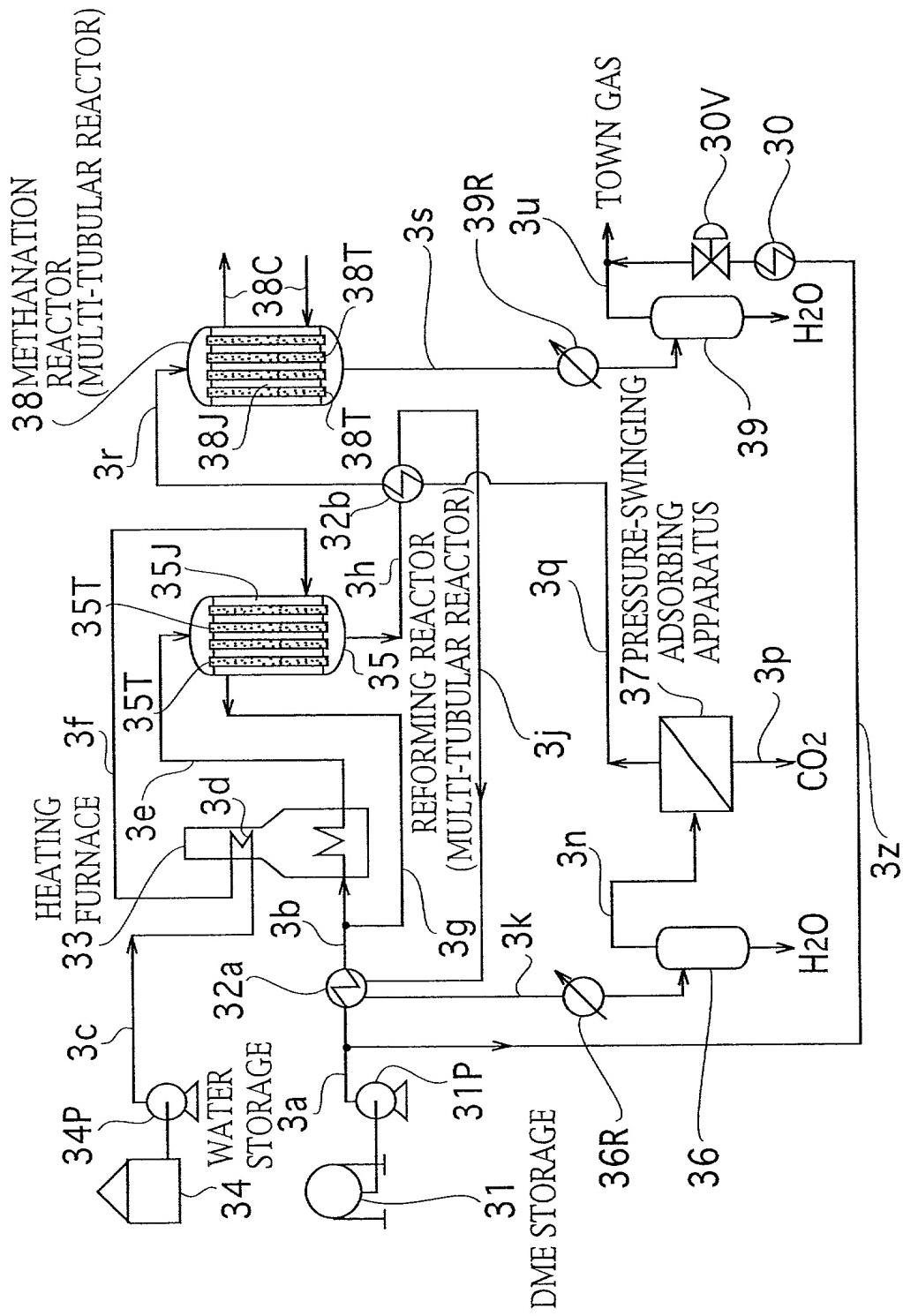


FIG. 2



09/980321

FIG. 3



Declaration and Power of Attorney For Patent Application

特許出願宣言書

Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣言する：

私の住所、郵便の宛先および国籍は、下欄に氏名に続いて記載したとおりであり。

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

Method for Producing Town Gas

その明細書を
(該当する方に印を付す)

ここに添付する。

12 May 2000 日に出願番号
第 PCT / JP00/03048 号として提出し、

_____ 日に補正した。
(該当する場合)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

私は、連邦規則法典第37部第1章第56条(a)項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

the specification of which

(check one)

is attached hereto

was filed on _____ as

Application Serial No. _____

and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

Japanese Language Declaration

私は、合衆国法典第35部第119条にもとづく下記の外国特許出願または発明者証出願の外国優先権利益を主張し、さらに優先権の主張に係わる基礎出願の出願日前の出願日を有する外国特許出願または発明者証出願を以下に明記する：

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior foreign applications

先の外国出願

Japanese Patent Application

No. 146943/1999, filed on May 26, 1999

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)
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Priority claimed

優先権の主張

<input checked="" type="checkbox"/> Yes あり	<input type="checkbox"/> No なし
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(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)
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(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)
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<input type="checkbox"/> Yes あり	<input type="checkbox"/> No なし
------------------------------------	-----------------------------------

私は、合衆国法典第35部第120条にもとづく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第35部第112条第1項に規定の態様で先の合衆国出願に開示されていない限度において、先の出願の出願日と本願の国内出願日またはPCT国際出願日の間に公表された連邦規則法典第37部第1章第56条(a)項に記載の所要の情報を開示すべき義務を有することを認め
る：

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

PCT / JP00/03048 12 May 2000

Pending

(Application Serial No.)

(出願番号)

(Filing Date)

(出願日)

(現況)

(特許済み、係属中、放棄済み)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(出願番号)

(Filing Date)

(出願日)

(現況)

(特許済み、係属中、放棄済み)

(Status)
(patented, pending, abandoned)

私は、ここに自己の知識にもとづいて行った陳述がすべて真実であり、自己の有する情報および信ずるところに従って行った陳述が真実であると信じ、さらに故意に虚偽の陳述等を行った場合、合衆国法典第18部第1001条により、罰金もしくは禁錮に処せられるか、またはこれらの刑が併科され、またかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損なうことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Declaration and Power of Attorney For Patent Application

特許出願宣言書 Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣誓する：

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名称の発明に關し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

Method for Producing Town Gas

その明細書を
(該当する方に印を付す)

ここに添付する。
 12 May 2000 日に出願番号

第 PCT/JP00/03048 号として提出し、
____ 日に補正した。
(該当する場合)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

私は、連邦規則法典第37部第1章第56条(a)項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

the specification of which

(check one)

is attached hereto.

was filed on _____ as

Application Serial No. _____

and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

Declaration and Power of Attorney For Patent Application

特許出願宣言書 Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣言する：

私の住所、郵便の宛先および国籍は、下欄に氏名に続いて記載したとおりであり。

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method for Producing Town Gas

その明細書を
(該当する方に印を付す)

ここに添付する。

12 May 2000 日に出願番号
PCT / JP00/03048 号として提出し、

____ 日に補正した。
(該当する場合)

the specification of which

(check one)

is attached hereto

was filed on _____ as

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Japanese Language Declaration

私は、合衆国法典第35部第119条にもとづく下記の外国特許出願または発明者証出願の外国優先権利益を主張し、さらに優先権の主張に係る基礎出願の出願日前の出願日を有する外国特許出願または発明者証出願を以下に明記する：

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior foreign applications

先の外国出願

Japanese Patent Application

No. 146943/1999, filed on May 26, 1999

(Number) (Country) (Day/Month/Year Filed)

(番号) (国名) (出願の年月日)

Priority claimed

優先権の主張

Yes あり No なし

Yes あり No なし

Yes あり No なし

(Number) (Country) (Day/Month/Year Filed)

(番号) (国名) (出願の年月日)

(Number) (Country) (Day/Month/Year Filed)

(番号) (国名) (出願の年月日)

私は、合衆国法典第35部第120条にもとづく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第35部第112条第1項に規定の態様で先の合衆国出願に開示されていない限度において、先の出願の出願日と本願の国内出願日またはPCT国際出願日の間に公表された連邦規則法典第37部第1章第56条(a)項に記載の所要の情報を開示すべき義務を有することを認め
る：

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application

PCT / JP 00/03048	12 May 2000	Pending
(Application Serial No.) (出願番号)	(Filing Date) (出願日)	(Status) (patented, pending, abandoned)
(Application Serial No.) (出願番号)	(Filing Date) (出願日)	(Status) (patented, pending, abandoned)

私は、ここに自己の知識にもとづいて行った陳述がすべて真実であり、自己の有する情報および信ずるところに従って行った陳述が真実であると信じ、さらに故意に虚偽の陳述等を行った場合、合衆国法典第18部第1001条により、罰金もしくは禁錮に処せられるか、またはこれらの刑が併科され、またかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損うことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration

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Prior foreign applications

先の外国出願

Japanese Patent Application

No. 146943/1999, filed on May 26, 1999

(Number) (Country) (Day/Month/Year Filed)

(番号) (国名) (出願の年月日)

Priority claimed

優先権の主張

Yes あり No なし

Yes あり No なし

Yes あり No なし

(Number)

(番号)

(Country)

(国名)

(Day/Month/Year Filed)

(出願の年月日)

(Number)

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(Country)

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PCT/JP00/03048 12 May 2000

Pending

(Application Serial No.)

(出願番号)

(Filing Date)

(出願日)

(現況)

(特許済み、係属中、放棄済み)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(出願番号)

(Filing Date)

(出願日)

(現況)

(特許済み、係属中、放棄済み)

(Status)

(patented, pending, abandoned)

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(代理人氏名および登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

Floyd B. Carothers, Reg. No. 24,252

CAROTHERS and CAROTHERS, Reg. No. 22,238

書類の送付先：

Send Correspondence to:

CAROTHERS and CAROTHERS
445 Fort Pitt Blvd, Suite 500
Pittsburgh, PA 15219

直通電話連絡先：(名称および電話番号)

Direct Telephone Calls to: (name and telephone number)

Floyd B. Carothers
(412)471-3575

唯一のまたは第一の発明者の氏名 <u>Yoshinori Mashiko</u>	Full name of sole or first inventor	
同発明者の署名 <u>J. Mashiko</u>	日付 <u>OCT. - 1, 2001</u>	Investor's signature Date
住所C/o JGC CORPORATION, 2-3-1, Yokohama-shi, Kanagawa-ken	Residence	
国籍 Japan	Citizenship	
郵便の宛先 same as residence	Post Office Address	
<u>J. Yoshimi</u>		
第2の共同発明者の氏名 (該当する場合) <u>Shoji Yoshimi</u>	Full name of second joint inventor, if any	
同第2発明者の署名 <u>J. Yoshimi</u>	日付 <u>OCT. - 1, 2001</u>	Second Inventor's signature Date
住所 c/o JGC CORPORATION, 2-3-1, Yokohama-shi, Kanagawa-ken	Residence	
国籍 Japan	Citizenship	
郵便の宛先 same as residence	Post Office Address	

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)

Page 3 of 3

Japanese Language Declaration

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Floyd B. Carothers
(412)471-3575

唯一のまたは第一の発明者の氏名 <u>Shinya Ishigaki</u>	Full name of sole or first inventor		
同発明者の筆名 <u>Ishigaki</u>	日付 <u>OCT. - 1. 2001</u>	Inventor's signature <u>Ishigaki</u>	Date <u>OCT. - 1. 2001</u>
住所 c/o JGC CORPORATION Research & Development Center, 2205, Narita-cho, Oarai-machi, Higashi Ibaraki-gun,	Residence 2205, Narita-cho, Oarai-machi, Higashi Ibaraki-gun,		
国籍 Japan	Citizenship JPX Ibaraki-ken		
郵便の宛先 Same as residence	Post Office Address		
第2の共同発明者の氏名(該当する場合) <u>Nobuhiro Yamada</u>	Full name of second joint inventor, if any		
同第2発明者の筆名 <u>N. Yamada</u>	日付 <u>OCT. - 1. 2001</u>	Second Inventor's signature <u>N. Yamada</u>	Date <u>OCT. - 1. 2001</u>
住所 c/o JGC CORPORATION Research & Development Center, 2205, Narita-cho, Oarai-machi, Higashi Ibaraki-gun,	Residence 2205, Narita-cho, Oarai-machi, Higashi Ibaraki-gun,		
国籍 Japan	Citizenship Ibaraki-ken		
郵便の宛先 same as residence	Post Office Address JPX		

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

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Floyd B. Carothers

(412)471-3575

唯一のまたは第一の発明者の氏名 <u>Mikio Yoneoka</u>	Full name of sole or first inventor
同発明者の署名 <u>mikio yoneoka</u>	Inventor's signature
住所 C/o Mitsubishi Gas Chemical Company, Inc. Niigata Research Laboratory	Date 11/09/01
国籍 Japan	Citizenship
郵便の宛先 same as residence	Post Office Address
JPX	
第2の共同発明者の氏名 (該当する場合) <u>Osamu Hashimoto</u>	Full name of second joint inventor, if any
同第2発明者の署名 <u>Osamu Hashimoto</u>	Second Inventor's signature
住所 C/o Mitsubishi Gas Chemical Company, Inc. Niigata Factory 3500, Matsuhama-cho, Niigata-shi, Niigata-ken	Date 07/09/01
国籍 Japan	Citizenship
郵便の宛先 same as residence	Post Office Address
JPX	

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Floyd B. Carothers
(412)471-3575

唯一のまたは第一の発明者の氏名 <u>Akira Ishiwada</u>	Full name of sole or first inventor
同発明者の署名 <u>AKIRA ISHIWADA 06/09/61</u>	Inventor's signature
住所C/O Mitsubishi Gas Chemical 2-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo	Residence
国籍 Japan	Citizenship
郵便の宛先 same as residence	Post Office Address
第2の共同発明者の氏名(該当する場合)	Full name of second joint inventor, if any
同第2発明者の署名 日付	Second Inventor's signature
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

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Floyd B. Carothers
(412)471-3575

唯一のまたは第一の発明者の氏名 <u>Hisashi Otsuka</u>	Full name of sole or first inventor
同発明者の署名 <u>Hisashi Otsuka</u>	Inventor's signature
住所 C/O ITOCHU Corporation Minato-ku, Tokyo	Residence
国籍 Japan	Citizenship
郵便の宛先 same as residence	Post Office Address
第2の共同発明者の氏名 (該当する場合)	Full name of second joint inventor, if any
同第2発明者の署名	Second Inventor's signature
住所	Residence
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